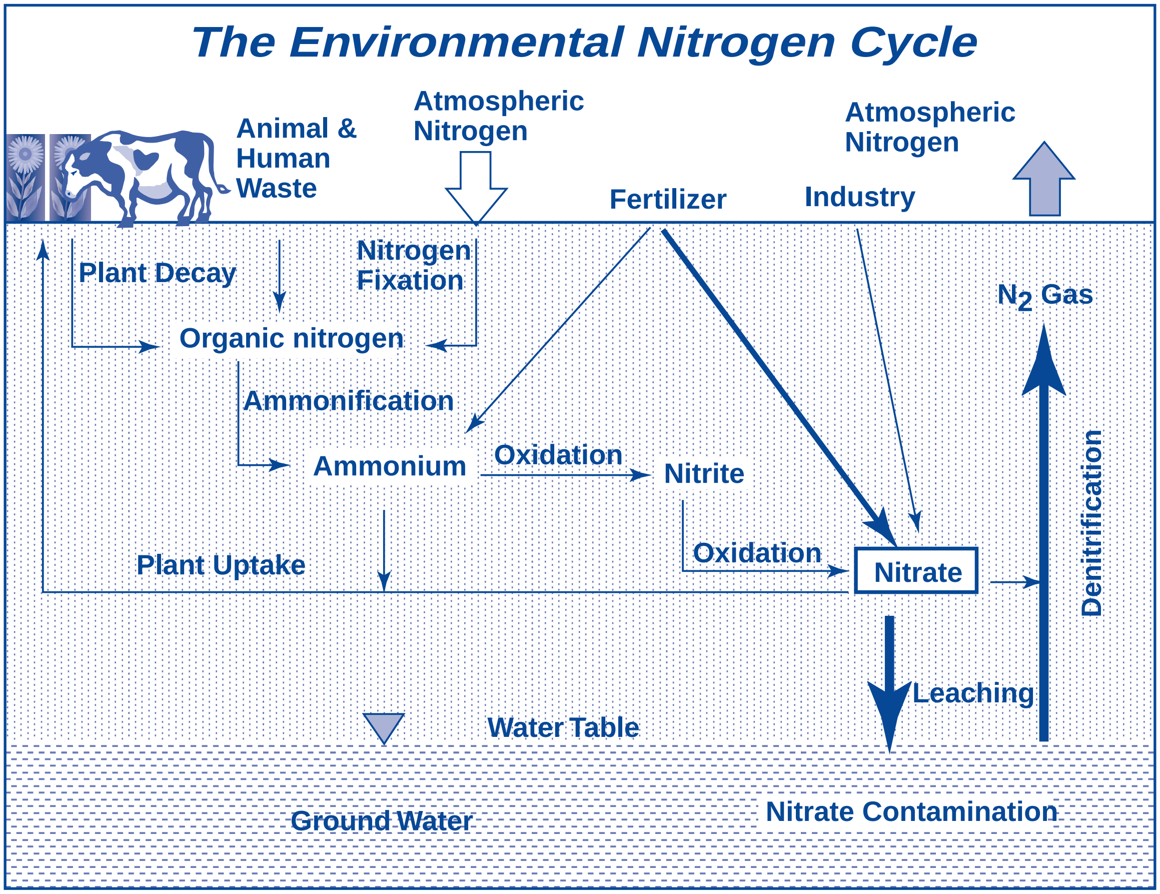
Technology Overview

Emerging Technologies for Enhanced *In Situ* Biodenitrification (EISBD) of Nitrate-Contaminated Ground Water


The Environmental Nitrogen Cycle

June 2000

Prepared by
Interstate Technology and Regulatory Cooperation Work Group
Enhanced *In Situ* Biodenitrification Work Team

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ACKNOWLEDGMENTS

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EXECUTIVE SUMMARY

Enhanced *in situ* biodenitrification (EISBD) is a developing technology for *in situ* reduction of nitrate in contaminated ground water. One of the most pervasive ground water contaminants in the U.S. is nitrate. This document focuses on issues related to environmental concerns about nitrate and current remediation techniques.

Traditional technologies for the remediation of nitrate-contaminated ground water are generally costly, lengthy, and often only partly effective. Of the emerging technologies for nitrate remediation, EISBD technologies offer a more cost-effective, timely, and more efficient means of reducing nitrate contamination to acceptable levels. This document describes two such EISBD technologies, their applicability to contaminated sites, and the results of the laboratory and field-testing done to date. Regulatory and stakeholder concerns related to both nitrate contamination and these two EISBD technologies are also presented.

Since methemoglobinemia (Blue Baby Syndrome) has been reported in several states and is associated with elevated levels of nitrate in drinking water, nitrate is a federally regulated compound. Nitrate contamination is also alleged to cause spontaneous, early-term abortions in humans and animals and may be related to certain types of cancer and thyroid dysfunction. Because of these issues, nitrate contamination is of concern to public health officials.

Sources of nitrate contamination include fertilizers, human and animal waste, and explosives. The presence of excess nitrate and other nutrients in streams, lakes, and estuaries has devastated fisheries and caused diminished recreational potential of the resource. One source of nitrate contamination in surface waters is nitrate-contaminated ground water.

Membership on this work team was open to all ITRC members. Participants with expertise or interest in nitrate treatment technologies in their states elected to join the team and contribute to the development of this work product. Professors from the University of New Mexico and University of Nebraska-Lincoln also participated and provided research information. ITRC public stakeholder representatives provided input regarding public and community concerns on the issues and remedial technologies.

The EISBD technology being developed at the University of New Mexico involves the injection of an amendment, usually acetate, through injection wells. These amendments are nontoxic, self-limiting, and promote the conditions optimal for anaerobic, microbial denitrification to occur. By amendment injection, the rate of denitrification is greatly accelerated, and nitrate is converted to nitrogen gas in a biochemical process. This technology has the potential of remediating sizable nitrate plumes in ground water systems.

The EISBD technology under development at the University of Nebraska-Lincoln is geared toward the reduction of nitrate contamination around public and/or domestic well fields dedicated to the production of drinking water. Injection of carbon amendments carefully calculated at controlled rates produce an environment where nonharmful anaerobic, nitrate-reducing microbes proliferate at a safe distance from the wellhead. Microbial denitrification reduces the nitrate concentrations, again through conversion to nitrogen gas.

TABLE OF CONTENTS

ACKNOWLEDGMENTS....................i

EXECUTIVE SUMMARY....................iii

1.0 INTRODUCTION....................1

2.0 SOURCES OF NITRATE....................2
  2.1 Human and Animal Wastes....................3
  2.2 Fertilizers....................4
  2.3 Explosives....................4
  2.4 Naturally Occurring Nitrates....................6
  2.5 Industrial Uses of Nitrate....................7

3.0 EFFECTS OF NITRATE....................7
  3.1 Human Health Effects....................7
  3.2 Human Exposure....................9
  3.3 Animal Health Effects....................11
  3.4 Environmental Effects....................11

4.0 TRADITIONAL NITRATE REMEDIATION OPTIONS....................12
  4.1 No Action....................12
  4.2 Pump with Beneficial Use....................12
  4.3 Pump and Treat....................13
  4.4 Pump and Waste....................13
  4.5 Phytoremediation....................13

5.0 NEW AND EMERGING REMEDIATION TECHNOLOGIES....................14
  5.1 Aboveground Denitrification....................14
  5.2 Permeable Reactive Barriers....................16
  5.3 Denitrification in Combination with Other Contaminants....................16

6.0 ENHANCED *IN SITU* BIODENITRIFICATION....................16
  6.1 General....................16
  6.2 Current Applications of Enhanced *In Situ* Biodenitrification....................17

7.0 RESEARCH AND DEVELOPMENT....................17
  7.1 UNM Professor Eric Nuttall....................17
  7.2 UNL Professor Roy Spalding....................24

8.0 REGULATORY ISSUES....................32
  8.1 Regulatory Enforcement of Nitrate Contamination....................32
  8.2 Issues Specific to Enhanced *In Situ* Biodenitrification....................34

9.0 PERFORMANCE PARAMETERS....39
9.1 Cost....39
9.2 Time to Completion....40
9.3 Contaminant Reduction....40

10.0 PUBLIC AND STAKEHOLDER ACCEPTANCE AND CONCERNS....40

11.0 CONCLUSIONS....41

12.0 REFERENCES....43

LIST OF TABLES

TABLE 1-1. Total Nitrogen Source Concentrations....7
TABLE 3-1. Number of Community Public Drinking Water Systems Found to be in Violation of the 10 mg/L Nitrate as Nitrogen MCL for the Years 1980 to 1998....10
TABLE 5-1. Nitrate Remediation Options....15
TABLE 7-1. Aboveground Denitrification Scale-Up Tests Using Indigenous Ground Water Bacteria....19
TABLE 7-2. Comparison of Average Denitrification Rates Using Acetate and TMP as Amendments....21

LIST OF FIGURES

FIGURE 1-1. The Nitrogen Cycle....2
FIGURE 2-1. Map of Areas with Major Explosives Contamination....5
FIGURE 2-2. USGS Nitrate Risk Map....6
FIGURE 7-1. Design of an *In Situ* Denitrification Test at Tri-Tech Site, Albuquerque's South Valley....20
FIGURE 7-2. Reaction Concentration Curves Resulting from Short-Term Monitoring during an *In Situ* Denitrification Test....21
FIGURE 7-3. Reaction Concentration Curves Measured During an *In Situ* Biodenitrification Test....22
FIGURE 7-4. Modified Schematic Diagram of Continuous Denitrification Field Test....22
FIGURE 7-5. Denitrification Results From 4-Inch Monitoring Well Using YSI 6920 Water Quality Monitor....23
FIGURE 7-6. Cross-Sectional View of Subsurface Entry Caisson, *In Situ* Microcosm, and Multilevel Samplers....24
FIGURE 7-7. Concentration vs. Time for Selected Analytes Involved in or Affected by Microbial Denitrification in a Microcosm Amended with 50 mg C L^{-1}....25

FIGURE 7-8. Concentration vs. Time for Selected Analytes Involved in or Affected by Microbial Denitrification Following Injection in a Microcosm Amended with 100 mg C L^{-1} 26
FIGURE 7-9. Layout of Daisy Injection System 29
FIGURE 7-10. Vertical Section of Daisy Injection System 30
FIGURE 7-11. Anion, D.O.C., and D.O. Concentration in Inner Well #3 31
FIGURE 7-12. Anion, D.O.C., and D.O. Under Pulse Injection in Extraction Well 31

APPENDICES

APPENDIX A Acronyms
APPENDIX B State Nitrate Ground Water Standards
APPENDIX C Nitrogen Compound Contamination Examples
APPENDIX D ITRC Work Team Contacts, ITRC Fact Sheet, ITRC Product List, and Document Evaluation Survey

EMERGING TECHNOLOGIES FOR ENHANCED *IN SITU* BIODENITRIFICATION (EISBD) OF NITRATE-CONTAMINATED GROUND WATER

1.0 INTRODUCTION

The purpose of ITRC is to improve environmental cleanup by encouraging use of innovative technologies, while reducing regulatory paperwork and overall costs. States are collaborating to develop and facilitate the use of standardized processes for the performance verification of new technologies.

The purpose of this document is to describe the pervasiveness of nitrate-contaminated ground water in the United States, create awareness associated with environmental and health problems, and provide an overview of the developing technology of EISBD. EISBD is an emerging technology for remediating nitrate-contaminated ground water and protecting public and domestic supply wells.

Nitrate is a worldwide water contaminant that can cause health problems in infants and animals and can lead to cultural eutrophication of natural water bodies (Fennessy and Cronk, 1997). The federally regulated Maximum Contaminant Level (MCL) in drinking water is 10 mg/l nitrate-nitrogen. This document describes nitrate in the environment, sources of nitrate, environmental and health effects of nitrate, current nitrate remediation practices, and the description of EISBD. Furthermore, current regulatory procedures and practices of nitrate-contaminated ground water and regulatory issues of EISBD will be discussed. Public concerns, issues, and awareness of nitrate contamination will be presented. Current research on EISBD will be presented along with performance and cost criteria for EISBD implementation.

The fate of nitrate is complex and includes several physical and biological processes of which denitrification plays a major role. There are four major forms of nitrogen in the soil and vadose zone: 1) Nitrogen gas, 2) Organic nitrogen, 3) Ammonia nitrogen bound on clays and aqueous in pore water, and 4) Nitrate. Denitrification results in the reduction of nitrate to nitrogen gas (Figure 1).

Nitrogen may be added to the soil through fertilizer, rain, animal and human waste, organic matter, and anthropogenic influences such as explosives and chemical wastes. Nitrogen may undergo chemical transformations before it is transported into ground water. The major divisions of the nitrogen cycle are mineralization, immobilization, nitrogen fixation, ammonification, nitrification, and denitrification. The conversion of mobile nitrogen species to some organic forms is termed immobilization or microbial and plant assimilation. Mineralization is the conversion of complex organic nitrogen to more simplified inorganic forms. Nitrogen may be present in the soil in the form of ammonia (NH_4^+). Ammonia may be metabolized by organisms, assimilated by plants, adsorbed by clay minerals and/or organic matter, and oxidized to nitrate (NO_3^-). Nitrification is the biochemical oxidation of ammonia to nitrate. In the presence of specific bacteria and oxygen, ammonia is enzymatically oxidized in a stepwise process to nitrite (NO_2^-) followed by nitrate (refer to equations on following page).

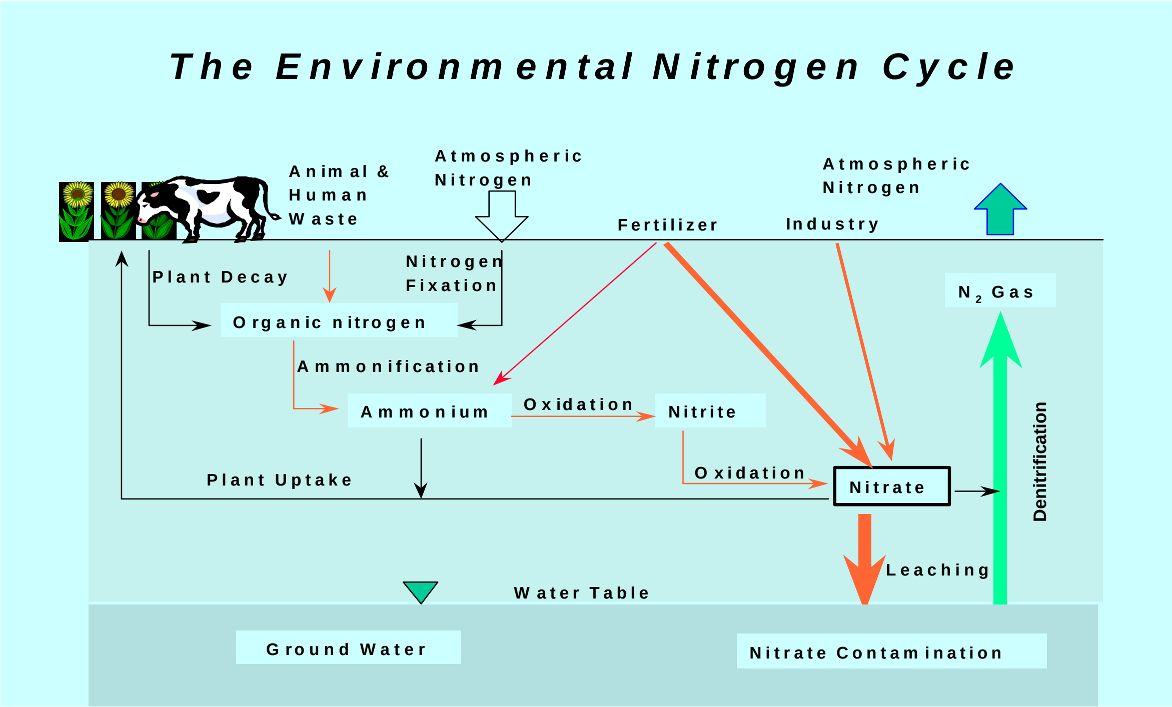

Figure 1-1: The Nitrogen Cycle (Deng, 1998)

$$RNH_2 + H_2 \longrightarrow NH_4^+ + \text{energy}$$

$$2NH_4 + 3O_2 \longrightarrow 2NO_2^- + 2H_2O + 4H + \text{energy}$$

$$2NO_2^- + O_2 \longrightarrow 2NO_3^- + \text{energy}$$

$$5C + 4NO_3^- + 2H_2O \longrightarrow 2N_2 + 4HCO_3 + CO_2$$

***R signifies an organic compound**

Nitrification will only occur in oxidizing environments. Secondary parameters affecting nitrification include temperature, moisture content, bacterial population of nitrifiers, and pH. Denitrification is the biochemical reduction of nitrate-nitrogen to nitrogen gas in the absence of oxygen. EISBD takes advantage of this naturally occurring process to remove nitrate contamination from ground water.

2.0 SOURCES OF NITRATE

Nitrogen losses due to denitrification help to maintain relatively low nitrate concentrations in ground and surface waters. In most naturally occurring environments, nitrate concentrations in ground water are usually < 3 mg/l (Smith et al., 1987). It should be pointed out that denitrification does occur naturally. Due to the Federal Clean Water Act, the EPA has established drinking water standards for nitrate at 10 mg/l nitrate-nitrogen. This standard applies to all public supply systems. Numerous states have established a ground water standard for nitrate (Appendix B). To provide a higher margin of health safety, Germany and South Africa have lowered their nitrate-nitrogen drinking water standards to 4.4 mg/l (Kross et al., 1995). Thailand has established a bottled drinking water standard for nitrate at 4.0 mg/l (Ministry of Public Health, 1981). Ground water concentrations of nitrate > 10 mg/l are attributed to various nitrogen sources. These sources are described below. Figure 2-2 reveals nitrate concentration trends across the United States.

2.1 Human and Animal Wastes

Waste produced by humans and animals are important sources of nitrate in any area characterized by significant human or animal populations. Nitrates from such waste can exhibit the characteristics of either point or nonpoint source pollution. Point sources occur at or near the actual waste facility involved and typically exhibit high levels of nitrate or ammonia in a limited area. Nonpoint sources are spread over large areas (e.g., in fertilization), and impacted aquifers are often characterized by lower (but still ≥ 10mg/l) levels of nitrate-nitrogen.

Nitrate from human waste originates mostly from individual septic systems or municipal wastewater treatment facilities. According to recent estimates shown on West Virginia University's Small Flows Clearinghouse Web site (http://www.nsfc.wvu.edu), approximately 25% of the population of the United States is served by individual systems such as septic tanks and cesspools. Typically, the nitrogen content of effluent from such systems is in the neighborhood of 30 to 60 mg/l total nitrogen, with ammonia making up the vast majority of this total (Minnesota Extension Service, 1994). The nitrogen content of this effluent varies widely depending upon the condition of the individual system and the type of waste being introduced. Traditionally, septic systems have served farms and rural businesses and have been of greatest concern in the more agricultural areas of the country. However, increasing development of non-farm acreage in the countryside bordering cities has resulted in a much greater density of onsite treatment systems (e.g., tens per square mile) than has historically been the case.

The remaining 75% of the U.S. population are served by municipal wastewater treatment systems. Again, nitrogen content of effluent from municipal systems will vary according to the nature of the incoming waste stream and the type and condition of the system. However, after primary treatment with activated sludge, the effluent typically still contains about 15 to 35 mg/l of total nitrogen; however, more advanced systems can reduce this to about 2 to 10 mg/l (EPA, 1993).

Waste from dairies, open feedlots, confined feeding operations, stockyards, and other facilities for raising and holding animals is also a potential source of nitrate and other forms of nitrogen. Recent public attention has focused on the operation of large hog confinement operations in places like North Carolina, Iowa, Colorado, and Nebraska; chicken and poultry farms in Arkansas and Missouri; cattle feedlots in Texas, Kansas, and Nebraska; and dairy farms in Wisconsin and the upper Midwest. While public concern over animal waste includes such issues as odor, flies, effects on property values, and surface water impact, these facilities represent a massive source of nitrogen and other nutrient inputs to ground water. For example, the University of Nebraska Cooperative Extension (1998) estimates suggest that waste from stock animals typically contains from about 0.045 to 0.18 Kg of nitrogen per pound of animal weight. Typically, total nitrogen concentrations of dairy wastewater range from 150 to 500 mg/l. In New Mexico alone, approximately one third of all dairy operations have contaminated ground water with nitrate above state ground water standards. In a study of three dairies in Merced and Stanislaus counties in California, maximum nitrate concentrations in ground water monitoring wells were 250 mg/l, and the average nitrate concentrations in ground water were 45 mg/l (Davis, 1995).

2.2 Fertilizers

Nitrogen is the most common element used as a fertilizer supplement for agricultural, turf, and garden use. Nitrogen fertilizer normally takes one of two forms: commercial fertilizer or animal waste. Animal waste has been applied to cropland for generations, both as a means of fertilization and waste disposal. Commercial fertilizer usage in the United States has become commonplace in the last half of the twentieth century with the advent of anhydrous ammonia, liquid nitrogen, and similar formulations that have greatly increased crop yields. In some cases, fertilizer has been over applied, either from a lack of understanding or good information about crop nutrient requirements, or as a relatively inexpensive “insurance policy” against unpredictable conditions that may leave crops short of nutrients. Nitrate’s high solubility and low sorptivity allows infiltration beyond the root zone when over applied or over watered. Thus, infiltration via precipitation or irrigation water easily transports nitrate, which is not taken up by plants, downward to ground water. As a result of this process, elevated ground water nitrate levels have occurred in heavily farmed areas. Results of federal, state, and local surveys, with over 200,000 nitrate data points, show large areas where ground water exceeds 10 mg/l in well drained soils that are dominated by irrigated cropland (Spalding and Exner, 1993). Recent attempts to reduce nonpoint nitrate contamination in ground water have focused on proper timing and reduced applications of fertilizer and irrigation water. Monitoring results from Nebraska and North Dakota indicate that such efforts can have a slow but positive effect on ground water nitrate levels.

Use of commercial fertilizers in agricultural areas has increased rapidly over the last three decades. Along with this explosion in usage went an explosion in the number of fertilizer distribution facilities. Until recently, commercial fertilizers were not recognized as a potential ground water contaminant. Even surface water scientists did not take seriously the threat of fertilizers until the 1970s. In addition, due to the low cost of commercial fertilizers, it has only been recently that distribution and sales facilities became overly concerned with good housekeeping practices as it related to fertilizer. Fertilizer sales facilities’ runoff was transported to ditches and then to surface waters or it infiltrated into the ground water system at these facilities in extremely high concentrations.

2.3 Explosives

Nitrogen is a major element in the manufacture of explosives, which primarily utilizes ammonium nitrate and diesel fuel. Without proper management and treatment, waste streams that contain high concentrations of ammonium nitrate and diesel fuel can cause ground water quality degradation. In some instances, this waste stream, along with improper handling of the ammonium nitrate, has created nitrate contamination. Presently, most explosive manufacturers have taken pollution prevention steps to reduce or eliminate this waste (due to regulations or economical savings). Waste streams from explosives manufacture contain nitrogen concentrations ranging from 200 mg/l to over 1,000 mg/l.

Ordnance testing grounds and weapons manufacturing, loading, packing, and transportation sites that were operated by or for DOE or DOD have historically used nitrogen compounds. The major nitrogen compounds that pose an environmental threat are 2,4,6 trinitrotoluene (TNT), 2,3,5-trinitro-1,3,5 triazine (RDX), and oxyhydro 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), (Townsend and Meyers, 1996). These compounds pose many environmental concerns in addition to nitrate contamination but may contribute to or are the source of nitrate-contaminated ground water. It is believed that since the manufacturing of these compounds utilize nitrogen compounds, nitrate may be present in high concentrations as residual compounds. Nitrate concentrations in ground water at these sites may range from 20 mg/l to over 200 mg/l. Figure 2-1 shows explosives sites that have contributed to contamination across the United States.

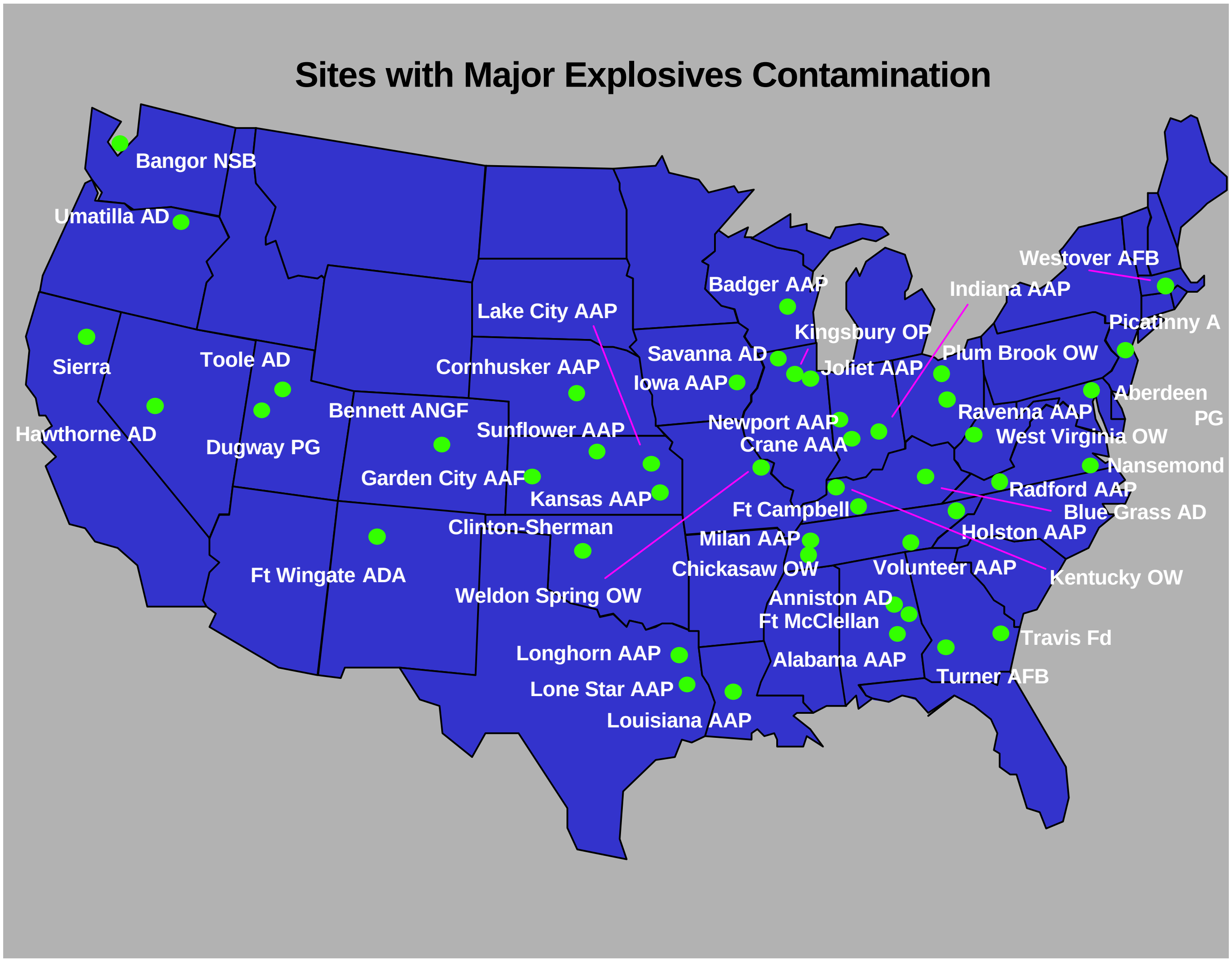

Figure 2-1. Map of Areas with Major Explosives Contamination (Note: DOD considers some of these sites to have been remediated)

2.4 Naturally Occurring Nitrates

It is unusual for pristine ground water systems to accumulate more than 3 mg/l nitrate (Madison and Brunnet, 1985). However, naturally occurring processes may cause nitrate contamination in ground water. One example occurred in Texas where the natural range consisted of buffalo grass that formed a symbiotic relationship with nitrogen-fixing bacteria. When these range lands were converted to dry land farming, the organic matter from the buffalo grass was oxidized to nitrate contamination in ground water at concentrations of 100 to 1,000 mg/l (Chapelle, 1993). The breaking up of prairie grasslands caused a huge flush of nitrate out of the root zone into ground water.

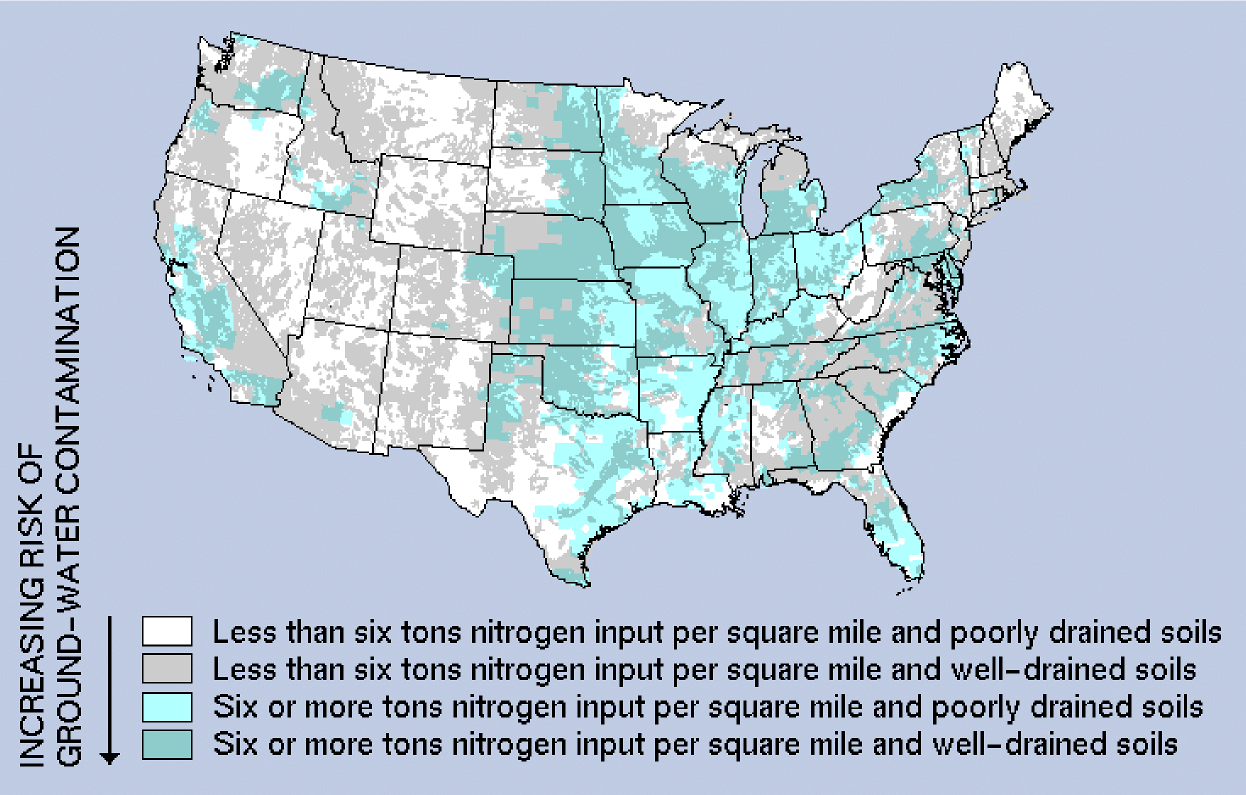

Figure 2-2. USGS Nitrate Risk Map, (Nitrate Elimination Co., Inc. Web site, 1999)

During lightning storms, atmospheric nitrogen is converted to nitrate and deposited to the soil through rain. In arid conditions, high nitrate concentrations may be caused by evapotranspiration of infiltrating rainwater in the shallow subsurface. During storm events, this high nitrate concentration may be transported to the shallow aquifer where nitrate concentrations in ground water are up to 60 mg/l (McQuillan, 1995).

Nitrate concentrations in ground water $\geq$ 10 mg/l may also be attributed to geologic formations. Sedimentary deposits with high organic matter may release nitrogen. In New Mexico, two limestone formations have been identified with naturally occurring ground water nitrate concentrations between 12–15 mg/l (Titus, 1980).

2.5 Industrial Uses of Nitrate

Nitrogen compounds are used extensively in industrial settings (examples provided in Figure 2-2). Some of the predominant nitrogen compounds used in industry are anhydrous ammonia, aqua ammonia, nitric acid, ammonium nitrate, ammonium nitrate solution, and urea. Some of the industrial uses are manufacturing of plastic and intermediates; metal processing; raw material in the textile industry; acid production; textile bleaching; petroleum refining; refrigeration; pulp, paper, and rubber production; as a catalytic agent in manufacturing processes; household cleaners; metal polishes; metal impurity extraction; fermentation processes, such as in the pharmaceutical industry; emulsifiers; slurries; water gels; cold packs for the medical field; adhesives, such as in the particle board industry; resins, such as in the cosmetic and fiberglass industries; deicing; and nitric acid used in many industries for various purposes. Nitrate contamination may result from the improper handling, disposal, and use of these compounds and varies in concentrations depending on the source (Potash Corp. Web site, 1999).

Table 1-1. Total Nitrogen Source Concentrations (MG/L)

SOURCE	TOTAL NITROGEN (MAX CONC. MG/L)
Human Waste (septic system)	100
Human Waste (PTOW)	80
Dairies (wastewater)	500
Animal Feed Lots (runoff, wastewater)	500
Hog Farms (wastewater)	?
Fertilizer Manufacturer (ground water)	10,000
Over Fertilized Croplands (ground water)	100
Explosives Manufacturer (ground water)	1,000
Munitions	500

(NOTE: Nitrogen is present in many different speciations dependent upon the source)

3.0 EFFECTS OF NITRATE

Nitrate concentrations in ground water $\geq$ 10 mg/l have many adverse effects on human and animal health and the environment. These effects are described below.

3.1 Human Health Effects

3.1.1 Methemoglobinemia

Methemoglobinemia, also known as Blue Baby Syndrome, is a disease generally resulting from the ingestion of high concentrations of nitrate in its inorganic form. In the stomach and small intestine of individuals with very low stomach acidity, indigenous bacteria chemically reduce the nitrate (NO_3^-) to nitrite (NO_2^-), a more reactive form of the compound. Nitrite is absorbed through the walls of the small intestine into the blood stream where it combines with hemoglobin to form methemoglobin. This process blocks the oxygen-carrying capability of the blood. When the concentration of methemoglobin becomes too high, the victim becomes cyanotic and can die of asphyxiation. The body does not have the capability to naturally change the methemoglobin back to effective hemoglobin. This condition especially occurs in infants below the age of six months while on a pure milk or infant formula diet. The cause of Blue Baby Syndrome is generally the mixing of infant formula with water containing high concentrations of nitrate (greater than 10 mg/l nitrate as nitrogen). Infants are not the only susceptible population, however. Children and adults suffering from maladies or treatments that lower the levels of stomach acid are also vulnerable to methemoglobinemia.

In 1984, an infant in Laurel, Nebraska was treated for Blue Baby Syndrome. The water used to mix her formula was shown to contain 66 to 80 mg/l nitrate as nitrogen (Mulvay, 1986). In 1986, an infant in South Dakota died as a result of ingesting water from a farm well containing approximately 150 mg/l nitrate as nitrogen (Meyer, 1994). In 1992, a six-week-old Wisconsin infant was diagnosed with methemoglobinemia on the second hospital admission. The contamination was traced to a shallow water supply well contaminated with 40 to 60 mg/l nitrate as nitrogen and up to 7.8 mg/l copper. It was concluded that the symptoms were caused by a synergistic effect of the nitrate and copper, an effect not previously recorded (Centers for Disease Control and Prevention, 1993). At least two cases of methemoglobinemia have been documented in New Mexico. One case occurred in an area of widespread septic-tank contamination in 1961. The other case occurred in an area contaminated by agricultural fertilization in 1980 (McQuillan, 1997). Two cases of methemoglobinemia from nitrate-contaminated private wells have been documented in South Dakota in 1981 and 1986 (Meyer, 1994). A 1982 survey of doctors in the Big Sioux River basin of South Dakota reported the occurrence of approximately 80 cases during the previous 30 years (Meyer, 1994).

Methemoglobinemia is not frequently diagnosed since it is not a required reportable disease in any state within the United States. And while better education and well construction techniques since the 1950s may account for a lowered incidence of the disease, another reason for it’s not being diagnosed may well be lack of medical training to recognize methemoglobinemia. According to several medical doctors in both North and South Dakota, medical students graduating in the last several years have not been trained to connect the symptoms of the disease with its possible source. Considering the lack of reporting requirements and medical recognition of the disease, there could well be many cases of methemoglobinemia that are not reported because it is no longer recognized.

3.1.2 Other Associated Effects

Although methemoglobinemia is the only disease that is currently directly attributable to elevated nitrate concentrations, there are other suspected negative health effects that have been potentially connected to this contaminant. Chief among them is the possibility of spontaneous abortions in women of childbearing age. A small study of these occurrences was carried out in LaGrange County, Indiana in 1993. Four women, living in residences served by private wells contaminated with nitrate ranging from 19 to 29 mg/l nitrate as nitrogen, experienced a total of eight spontaneous abortions. Three of the women lived within one mile of a point source of nitrate contamination. One of the women had four spontaneous abortions within the first 8 to 11 weeks of her pregnancies. At least one of these women had previously carried a child to term. The fourth woman resided approximately 10 miles from the first three. She had previously carried four babies to healthy births but had two spontaneous abortions in 1994. The home's water supply contained an average nitrate as nitrogen concentration of 29 mg/l. After switching to nitrate free drinking water, all four women carried babies to term (Centers for Disease Control and Prevention, 1996).

Another health concern, which has been under study for many years, is nitrate-contaminated drinking water's link to non-Hodgkin's lymphoma and stomach cancer. Although this link is very tenuous and controversial, research and surveys are ongoing in an attempt to document the connection. A recent article discussed the rise in incidence and mortality rates for non-Hodgkin's lymphoma (Blair et al., 1997). The authors note that the rising trend is seen in all histologic types and all ages except for the very young. In further support of this potential link, they note that the rates are rising faster in rural than in urban areas. They have determined that this upward trend began approximately in the 1960s and suggest that this trend points toward environmental factors as a possible cause. They indicate that the research is hampered due to the poorly understood etiology of the disease. Several avenues of approach are being pursued. One of the links that have been found so far is that two specific types of this related cancer are more prevalent in farmers and others who work in close contact with animals and animal products.

Nitrate is identified as a possible cancer risk due to its transformations in the body. Approximately 5% of ingested nitrate is converted to nitrite, which can then combine with organic compounds to form N-nitroso compounds, which have been shown to be potent animal and human carcinogens (Blair et al., 1997). An ecological study in China was also cited as showing a possible link between nitrate and leukemia mortality rates (Wu et al., 1993). Another study in Nebraska (Weisenburger, 1991) showed a slightly positive correlation between high nitrate concentrations in water supplies and non-Hodgkin's lymphoma.

3.2 Human Exposure

Nitrate is likely the most ubiquitous ground water contaminant in North America. EPA estimates that 2.4% of private wells exceed 10 mg/l nitrate concentrations as a national average (EPA, 1992). A 1994 study of Midwestern states showed that 13.4% of domestic well samples exceed the nitrate standard (CDCP, 1998). A study of 268 wells in southeast Nebraska showed 71% of the wells exceeded the standard (Meyer, 1994).

In North Dakota, nitrate testing of potable water samples has been ongoing for more than 40 years. A database constructed of private water supply samples through the late 1980s showed that 11% of the samples submitted exceeded the 10 mg/l nitrate as nitrogen standard. Of the 25,000 samples in the database, over 1% exceeded 100 mg/l. It is the Department of Health's practice to contact those people who submitted extremely high nitrate samples, both as a warning gesture and to determine the source of the nitrate contamination in the well. While many of the incidents of high-nitrate contamination can be directly traced to poor well location and construction, there are still a sizable number of cases where it has been impossible to determine the source of nitrate or the pathway of contamination. Many times, the Department of Health Laboratory reports nitrate concentrations in excess of 200 mg/l nitrate as nitrogen. These occurrences are not always in shallow ground water. Properly constructed wells up to 275 feet deep have been identified with extremely high nitrate concentrations.

The concern of private domestic well contamination has become a public issue in numerous states. Recently, legislators from New Jersey voted to require testing of private wells before the sale of homes. The bill will also require homes that are leased for longer than one year to be tested for bacteria and nitrates (*Garden State EnviroNews*, 1999).

Nitrate is a major concern for public drinking water systems. The Safe Drinking Water Act of 1974 listed nitrate as one of the primary drinking water contaminants of concern and subsequently set the 10 mg/l nitrate as nitrogen MCL. As the program became organized, records began to be kept.

Table 3-1. Number of Community Public Drinking Water Systems Found to be in Violation of the 10 mg/L Nitrate as Nitrogen MCL for the Years 1980 to 1998.

Year	Community Nitrate MCL Violations			Community System Totals	
	Number of Individual Violations	Number of Systems in Violation	Population Affected	Total Number of Reporting Systems	Total Population Served
1998	372	188	747,805	54,367	252,530,574
1997	361	191	369,327	54,674	248,925,715
1996	441	238	576,633	55,420	246,623,730
1995	390	234	469,855	55,633	243,566,000
1994	534	284	310,403	56,747	243,049,000
1993	473	287	639,684	57,561	242,679,000
1992	373	227	451,731	58,666	245,183,000
1991	375	227	414,575	59,266	232,562,000
1990	425	241	472,890	59,182	242,048,000
1989	425	262	793,017	59,117	222,581,000
1988	502	291	968,883	58,099	218,827,000
1987	521	313	776,725	58,908	226,000,000
1986	572	304	878,975	58,557	219,000,000
1985	564	338	818,721	58,500	
1984	562	317	806,153	58,300	
1983	580	286	467,091	58,700	
1982	532	317	727,318	58,900	
1981	417	282	1,565,805	58,919	
1980	367	257	580,347	63,975	

The table above lists the number of violations issued in community public drinking water systems from 1980 through 1998 (Abe Siegel, EPA, Information Services, SDWIS, 1999, personal communication.). While the table is quite straight forward, one thing should be clarified. The second and third columns list the number of individual nitrate violations and the number of community public drinking water systems in violation, respectively. Once a community drinking water system is found to be in violation of the act, each additional sampling above the MCL may be counted as an additional violation, and the system is required to resample on a specified schedule until it returns to compliance with the act. Thus, any one public drinking water system may accumulate more than one violation per year (see columns two and three in Table 3-1).

Monitoring data from 21 state drinking water regulatory agencies showed that over 1,000 water suppliers reported at least one well or tap water sample above the nitrate MCL. (Pouring it on, 1996). In New Mexico alone, 81 public water supply wells have exceeded the MCL (McQuillan et al., 1999).

3.3 Animal Health Effects

Water quality related to animal health has been an issue since the 1970s. Livestock may develop health problems due to poor water quality. Nitrate-contaminated water consumed by livestock has resulted in nitrate poisoning. At high enough nitrate concentrations (> 300 mg/l), nitrate poisoning may result in animal death. At lower concentrations, nitrate poisoning can increase the incidence of still born calves, abortions, retained placenta, cystic ovaries, lower milk production, reduced weight gains, and vitamin A deficiency. Livestock may be harmed at nitrate-nitrogen concentrations between 100 to 300 mg/l, and nitrate poisoning in cattle, sheep, and horses may occur at concentrations > 300 NO_3-N. Recommended limits of nitrate in drinking water for livestock and poultry should not exceed 100 mg/l. The accurate assessment of the source of nitrate poisoning is difficult because if the diet includes crops prone to nitrate accumulation, nitrite accumulation in the animal may occur (Meyer, 1990; Kvasnicka et al., 1990; and Faries et al., 1991).

3.4 Environmental Effects

Nitrogen compounds in concentrations exceeding background levels (3 mg/l) in surface waters reflect pollution from domestic, industrial, or agricultural sources (Smith et al., 1987). Since the early 1970s, trends show an increase in nitrate concentrations in rivers and streams of the Midwest. Nitrogen and phosphorous are the two most important nutrients limiting primary productivity; excessive inputs of nitrogen and phosphorous increase the rate of eutrophication in lakes and impoundments (Cole, 1983). While nitrogen and phosphorous (nutrients) from municipal wastes has been significantly reduced, nitrogen compounds from nonpoint sources may prevent achievement of the nation’s water quality goals established by the Clean Water Act in 1972 (Smith et al., 1987).

The effects of nutrient loading on water quality and productivity are particularly important for impoundments and natural lakes, which are often sources for municipal water supplies and water-based recreation (Kimmel, 1981). Levels of nitrate much lower than the MCL for drinking water contribute to increased rates of eutrophication in surface waters (Cole, 1983).

Runoff from row-cropped agricultural fields and feedlots is significantly higher than from pastureland (Beaulac and Reckhow, 1982). In a national study, increased N loading to runoff from cropped lands was associated with increased nitrogen fertilization rates, which amounted to a 68% increase from 1970 to 1981 on cultivated lands (Smith et al., 1987). Runoff from animal feedlots provides high concentrations of nitrate and ammonia (Beaulac and Reckhow, 1982).

Wetlands and forested areas are our prime defenses for trapping and purifying nutrients in runoff before they enter streams (Fennessy and Cronk, 1993-1997). If nitrate loading to coastal streams and rivers occurs, it generally stimulates algal blooms in salt-water estuaries and bays. In the Gulf of Mexico, nitrate runoff from the Mississippi River has resulted in up to a 7,032 square mile hypoxia zone (Rabalais et al., in press). In Chesapeake Bay rivers, animal waste-N is believed to be the cause of a deadly Pfisteria bloom in the summer of 1998 (Burkholder and Glasgow Jr., 1997).

4.0 TRADITIONAL NITRATE REMEDIATION OPTIONS

Ground water remediation of nitrate contamination has not received as much attention as known carcinogenic contaminants. Remediation of these nitrate plumes has not been as common or extensive as other contaminants of concern. However, when a ground water nitrate plume has been identified, certain corrective remediation activities have been employed. Site-specific information has determined which remediation option to employ. The following subsections describe remediation activities identified by the EISBD Work Team. Note that most remediation options involve pumping of contaminated ground water.

4.1 No Action

For various reasons, no remediation action for nitrate-contaminated ground water has been a common approach and perhaps the option most often chosen. Some reasons for no action are public awareness, extent of contamination, inconsistent regulatory enforcement, economic issues, and responsible parties who are unable to pay for remediation. When a supply well is impacted with nitrate contamination, certain institutional actions are taken to provide clean water without addressing the contamination. Examples of this are deepening the supply well to find clean water, blending the contaminated water with clean water to meet standards, or supplying an alternate water supply. If no action is taken, ground water nitrate plumes remain and may continue to increase in concentration and size, posing a continued or greater threat.

4.2 Pump with Beneficial Use

Pumping and using nitrate-contaminated ground water has been the most common remediation technique employed after no action. This remediation usually entails pumping large volumes of contaminated water and directly applying it onto croplands. Crops remove nitrates from the root zone for growth. The crops are then harvested, and the nitrates are removed from the environment. There are numerous disadvantages to this remediation technique:

- Large costs
- Considerable engineering and planning to extract and deliver the contaminated water
- Possibility of further nitrate contamination
- Securing water rights

- Developing appropriate land use for crop application
- Regulatory permitting

In addition, the pump and use of nitrate-contaminated ground water may be employed in other industries, such as the construction industry. The contaminated water may also be used as a mixer with fertilizers for application on crops.

4.3 Pump and Treat

Pumping and treating nitrate-contaminated ground water is another remediation technique often employed. This option is usually employed at public supply well heads and may not address the nitrate plume. The treatment of the nitrate-contaminated ground water may be through wastewater treatment plants, construction of a treatment plant, reverse osmosis, ion exchange, or electrodiolysis. Nitrate-contaminated ground water is pumped and discharged to existing wastewater treatment plants for nitrate removal, or specific treatment plants are constructed to address the nitrate contamination. This treatment may be expensive, and existing treatment plans may not be able to handle the increased volume. Ion exchange involves pumping nitrate-contaminated water through a resin bed containing strong base anion exchange resin, whereby nitrate is exchanged for chloride or bicarbonate. In reverse osmosis, nitrate is removed by forcing the water across a semipermeable membrane and leaving nitrate and other ions behind. A reverse osmosis waste stream needs to be treated and disposed from this system. In electrodyolisis, ions are transferred through membranes from a less concentrated to a concentrated solution due to the passage of a direct electric current. This process is expensive and requires close monitoring (Kappor, 1997).

4.4 Pump and Waste

Pumping nitrate-contaminated ground water to waste has also been employed, although this is usually not encouraged. The nitrate-rich water may be discharged to a contained evaporation system or injected into a deep saline aquifer or geologic unit. Ground water resources are lost to evaporation or injection. Disposal of the evaporate may be a problem if improperly managed. It would not be prudent to move a contaminant source to a noncontaminated location. The injection of nitrate-contaminated ground water into a deep geologic unit poses many uncertainties.

4.5 Phytoremediation

Phytoremediation is a means of removing, transforming, or binding contaminants in soil and ground water through the use of plants, both as active and passive remediation tools. Plants can remediate contaminants through one or more of four processes: phytotransformation, phytoextraction, phytostabilization, and rhizofiltration (Schnoor, 1997). Of these, phytotransformation is the process most active in plant removal of nitrogen compounds of interest. In addition to their ability to transform nitrogen compounds, some plants transpire great quantities of water. Thus, not only can plants remove certain types of contaminants, they can also act as ground water extraction and flow control structures. In addition, phytoremediation techniques generally meet with public acceptance due to the ease of understanding and a desire to see living things transform a contaminated site.

In 1987, a University of Iowa team effectively demonstrated the potential of phytoremediation for nitrate removal. They planted a buffer strip of poplar trees between a stream and a corn field from which nitrate was leaching into a stream. By 1990, when the trees were three years old, they were effectively reducing nitrate-nitrogen from 35 mg/l to 3 mg/l in ground water leaving the cornfield (Licht and Schnoor, 1993). Since that time, many fertilizer-contaminated sites have initiated phytoremediation, although very little concerning this contaminant remediation has appeared in the literature. Several fertilizer sales facilities in North and South Dakota (Communication with Gary Haag, SD Dept. of the Environment, 1997) have implemented phytoremediation since then, at least as part of contaminant remediation strategies. Hybrid poplar, cottonwood, and willow tree plantings have figured prominently in some sites. In others, traffic and other restrictions have led to plantings of other high nitrogen and water-consuming plant species, such as alfalfa (even though it also fixes atmospheric nitrogen) and reed canary grass. Low, deep-rooted hedges have been suggested in other areas where visibility is an issue.

While this technique is a highly effective means of dealing with fertilizer and other nitrogen compound contamination, there are limits to its application. High concentrations of nitrate and/or ammonia can result in plant toxicity, either overall or at certain developmental stages of the plant. Alkaline or saline soils may also prove toxic, as may the presence of other contaminants. Depth of contamination may exceed the rooting depth of plants, thus also limiting the application, though some sites show that nitrogen uptake and transpiration can dramatically alter contaminant patterns at depths up to 10 meters below ground. Heavy, tight soils may limit rooting depth as well, even with species that are normally deep rooted, as can poorly drained soil conditions. Traffic patterns, property boundaries, right-of-ways, building proximity, and deed restrictions may also prove to be limiting issues, as can regulatory prejudice. Another potentially limiting factor in the decision to employ phytoremediation is the length of time it takes plantings to mature sufficiently to become effective at significant nitrogen removal. Sites that demand immediate action to protect drinking water supplies may not be able to wait for maturation of a planting. While many of these issues can be overcome, there is still a good deal of research needed before we will see this technology used to its maximum potential.

5.0 NEW AND EMERGING REMEDIATION TECHNOLOGIES

Remediation of nitrate contamination has recently received renewed interest. The EISBD Work Team has identified some of the new and emerging remediation technologies that address denitrification. These new technologies are summarized on the next page.

5.1 Aboveground Denitrification

Due to the pervasiveness of nitrate-contaminated ground water and its impact on public supply wells, research has been conducted to biochemically denitrify water aboveground. This process takes advantage of biodenitrification and is accomplished by pumping nitrate-contaminated ground water into packed tower biofilm columns. Denitrifying bacteria and a carbon source are added to the columns to stimulate the denitrification process (see Section 6.1). This process has recently become commercially available (Silverstein, 1997).

Table 5-1. Nitrate Remediation Options

Remediation Technology	Basic Methodology	Benefits	Concerns
No Action	Monitoring of ground water	• no equipment cost • no clean up cost or efforts • dilution to meet standard	• increase in plume size • impact on receptors • violation of standard
Pump and Use	Impacted ground water pumped and used	• plume containment • mass removal • beneficial use of extracted water	• long-term • engineering cost • water rights issues • regulatory permitting
Pump and Treat	Impacted ground water pumped and treated	• plume containment • mass removal • re-use of clean water • injection of clean water	• long-term • engineering cost • water rights issues • treatment system • potentially expensive • hazardous concentrated waste stream
Pump and Waste	Impacted ground water pumped and wasted	• plume containment • mass removal	• long-term • considerable engineering cost • potential plume migration • water rights issues • regulatory issues
Phytoremediation	Impacted ground water treated by plant uptake	• plume containment • low cost • aesthetically pleasing	• depth to water is a limiting factor • land requirements • property rights • long-term • management of plants
Aboveground Denitrification	Impacted ground water pumped to bioreactors, treated, and distributed	• treated to below standards • new ex situ treatment of nitrate contamination	• size of bioreactors may be a factor • maintaining stable temperature • treats pumped water and doesn't address contaminant plume
Denitrification in Combination with Other Contaminants	During anaerobic bioremediation of other organic contaminants, nitrates serve as an electron acceptor	• fortuitous nitrate reduction in the presence of other organic contaminants • if nitrate is present in an organic contaminant plume, and conditions are anaerobic, denitrification most likely will occur	• reducing conditions must be present • a carbon source must be present • monitoring to determine denitrification must be ascertained
Enhanced In Situ Biodenitrification	Impacted ground water amended to stimulate biochemical reaction to convert nitrate to nitrogen gas	• cheap • very fast • natural process • complete plume remediation • new technology	• impact to geochemistry • regulatory concerns • biomass build up

5.2 Permeable Reactive Barriers

Permeable reactive barriers (PRBs) are currently being researched for their application to denitrify contaminated ground water. Los Alamos National Laboratory in cooperation with the University of New Mexico is studying the feasibility of denitrifying reactive barriers. These PRBs have the potential to contain or remediate a nitrate plume before any receptors are reached.

5.3 Denitrification in Combination with Other Contaminants

As described in the nitrogen cycle, denitrification occurs naturally, however, usually at very low rates unless an abundant carbon source is present. One example is a grain silo facility contaminated with carbon tetrachloride (CT) and nitrate. A gasoline plume commingled with the CT and nitrate. The carbon-containing gasoline compounds created anaerobic conditions whereby nitrate was the electron acceptor, and the compounds in the gasoline were the electron donors. The CT was subsequently mineralized with the residual nitrate continuing to serve as an electron donor (McQuillan et al., 1998). For many documented gasoline plumes in the presence of a nitrate plume, denitrification occurs along with bioremediation of the gasoline. The introduction of nitrate into gasoline plumes has been proposed to encourage anaerobic bioremediation of the gasoline.

6.0 ENHANCED *IN SITU* BIODENITRIFICATION

6.1 General

The understanding of denitrification is essential for the application of enhanced *in situ* biodenitrification. The nitrogen cycle describes the processes that involve organic nitrogen. Each one of these processes is a bacterial biological process. Organic nitrogen is converted to ammonia through ammonification; ammonia is converted to nitrate through nitrification in the presence of oxygen; and nitrate is converted to nitrogen gas through denitrification in the absence of oxygen. The denitrification process is not a direct conversion to nitrogen gas (g) but a multistep process described below.

$$\mathbf{NO_3 \longrightarrow NO_2 \longrightarrow NO\ (g) \longrightarrow N_2O \longrightarrow N_2\ (g)}$$

Microbial populations responsible for bioremediation require a source of carbon, an electron donor, an electron acceptor, appropriate nutrients, a suitable temperature range, pH, and other environmental conditions. Very often the carbon source serves as the electron donor. Enhanced *in situ* bioremediation systems stimulate the biodegradation of certain contaminants by manipulating these requirements in the subsurface.

Nitrate reduction occurs during anaerobic respiration. In the absence of oxygen and the presence of a carbon source (bacterial food source), bacteria utilize the nitrate as an electron acceptor during respiration. The nitrate is converted to nitrite, whereby anaerobic respiration continues with the formation of innocuous nitrogen gas.

Enhanced *in situ* biodenitrification is a remediation technology through which a carbon source is introduced to a nitrate-contaminated aquifer. Since most aquifers are aerobic, indigenous aerobic bacteria utilize the introduced carbon as a carbon source and oxygen as the electron acceptor. Oxygen in the aquifer becomes depleted, forming an anaerobic aquifer. When this occurs and an abundant carbon source is present, indigenous denitrifying bacteria proliferate and reduce nitrate to nitrogen gas through anaerobic respiration (Figure 1-1).

6.2 Current Applications of Enhanced *In Situ* Biodenitrification

EISBD technologies have until recently not been commercially available. Certain research projects and field tests of technologies have been conducted. The University of New Mexico has completed laboratory and field pilot tests for remediation of a nitrate plume. Due to UNM's EISBD success to date, UNM has recently licensed this technology to Key Technologies, Inc. of Albuquerque, New Mexico (Dr. Alan Kuhn, President). The University of Nebraska-Lincoln has completed laboratory and field pilot tests for protection of public supply wells. Initial research results are most promising.

Further research is being conducted for *in situ* denitrification. The Pacific Northwest National Laboratory has been conducting bench-scale testing of vegetable oil as a carbon source in bioreactors and soil columns to denitrify amended water (Fredrickson, 1998). Biodenitrification microcosm studies have been conducted at the University of Nebraska-Lincoln that showed considerable nitrate removal (Dahab et al., 1991). A review study conducted in 1992 described numerous laboratory studies of denitrification rates from aquifer samples (Korom, 1992). Experimental studies conducted in Great Britain using a designed flow-through microcosm apparatus showed that denitrification in a sandstone aquifer material could be increased and controlled by supplying a carbon source (Clark et al., 1993-1999). Ongoing research of autotrophic denitrification indicates that nitrate is reduced to nitrogen gas in the presence of iron and sulfate in anaerobic conditions. Thermodynamic conditions show that nitrate can serve as an electron acceptor, and reduced inorganic species such as Mn^{2+}, Fe^{2+}, and HS^- can serve as electron donors (Korom, 1992) and (Kappor, 1997). The EISBD Work Team has not completed a comprehensive literature search for all denitrification studies and applications that may be ongoing.

7.0 RESEARCH AND DEVELOPMENT

7.1 UNM Professor Eric Nuttall

Abstract: An *in situ* ground water denitrification process was developed using a series of increasingly larger scale tests, starting from microcosm-scale experiments through pilot-scale tests and finally a field demonstration. Indigenous soil and ground water denitrifying bacteria were stimulated using sodium acetate as a carbon substrate and trimetaphosphate as a nutrient. *In situ* denitrification was successfully demonstrated using a push-pull test and a small-scale continuous field test at a New Mexico site in Albuquerque's South Valley. Ground water parameters of pH, Eh, conductivity, and concentrations of dissolved oxygen, nitrate, nitrite, acetate, sulfate, and bromide were measured. Results showed that the high toxic levels of nitrate (100 mg/l nitrate-nitrogen) were metabolically transformed into harmless nitrogen gas within three to five days, and the nitrate concentration was reduced to below 1 mg/l. The final pH, Eh, and conductivity values of ground water were not significantly changed during the process.

Introduction: Nitrate contamination in drinking water poses serious health effects to both humans and animals. Infants are most seriously impacted. Blue Baby Syndrome (methemoglobinemia) is potentially fatal when infants (from birth to six months) drink contaminated water at nitrate levels above the MCL (10 mg/l nitrate-nitrogen). Other reported diseases caused by drinking water polluted with nitrate include cancer, disruption of thyroid function, and birth defects. Nitrate contamination in ground water is most commonly caused by overfertilization of agricultural crops, improper disposal of animal and human waste, and industrial liquid waste.

Remediation of nitrate-contaminated ground water and soils can occur under certain conditions by natural bioremediation. Nature has evolved indigenous denitrifying bacteria capable of converting nitrates found in subsurface environments, i.e. soils and ground water, into harmless nitrogen gas (Payne, 1981); however, the process is often very slow, requiring decades or centuries to complete due to the lack of a carbon energy source for bacterial growth. Enhanced or accelerated biodenitrification is accomplished by stimulating indigenous denitrifying bacteria through the addition of a suitable carbon energy source (McCarty et al., 1969). Carbon substrates, such as methanol, ethanol, acetate, and sugar can significantly enhance denitrification rates by serving as electron donor and energy supply for the indigenous bacteria while nitrate is the electron acceptor. In the metabolic denitrification process, nitrate is transformed into the final product of nitrogen gas via a multistep chemical reduction: $NO_3^- \rightarrow NO_2^- \rightarrow NO\ (g) \rightarrow N_2O\ (g) \rightarrow N_2\ (g)$ (Knowles, 1982). Usually, it is found that nitrite is the most significant intermediate while NO and N_2O are short-lived. In practice, the dissolved oxygen is also an electron acceptor and must be removed by bacteria prior to denitrification. The stoichiometric chemical reaction for de-oxygenation is described in equation (1), in which we assume that 30% of carbon is consumed for the cell synthesis (Deng, 1998). The stoichiometric relation describing denitrification using acetate was experimentally derived (equation 2) (Lu, 1998) and indicates that most of the carbon source (90%) is used to provide energy for the bacteria rather than biomass production.

$$\mathbf{O_2 + 0.816\ CH_3COO^- + 0.103\ NO_3^- + 0.964\ H^+ \rightarrow 0.103C_5H_7O_2N + 1.207\ CO_2 + 1.413\ H_2O} \tag{1}$$

$$\mathbf{NO_3^- + 0.712\ CH_3COO^- \rightarrow 0.485\ N_2 + 0.03\ C_5H_7O_2N + 1.273\ HCO_3^- + 0.106\ H_2O + 0.44\ OH^-} \tag{2}$$

[Where $C_5H_7O_2N$ represents the cell formula.]

Because enhanced denitrification is rapid and can be applied *in situ*, it appears likely to be a cost-effective technology for treating ground water and soils. Many denitrification studies (Kappelhof, et al., 1992; Green et al., 1994) have investigated *ex situ* biodenitrifying reactor systems; however, only a few studies have investigated *in situ* biodenitrification (Mercado et al., 1988; Hamon and Fustec, 1991).

Objective: The objective of this study is to determine the feasibility of *in situ* biological denitrification at a site in New Mexico (Nuttall et al., 1997, Nuttall, 1997, Deng et al., 1998, Abdelouas et al., 1998). The approach was to scale up the process in a series of batch microcosm experiments in closed reactors ranging in volume from 0.16 L to 4542 L (1200 gal). Following successful completion of the *ex situ* tests, an *in situ* denitrification experiment was performed.

Site Description: The *in situ* denitrification site in Albuquerque, New Mexico's South Valley is a 40-year-old nitrate plume covering an area of about 220 hectares and a volume of 6.4 billion liters. Ground water contamination was caused by over fertilization at a vegetable farm in the 1950s. The water table is at a depth of 22 meters, and the top of the aquifer contains a 10-meter nitrate contamination zone. The plume is moving very slowly in a sandy/loam soil aquifer with a hydraulic conductivity of about 10^{-3} cm/sec. The average nitrate-nitrogen concentration in the ground water is 90–110 mg/l. The ground water pH is 7.4–7.7 with a temperature of 20^{o}C. At this site in 1980, a Blue Baby Syndrome incident was reported.

Experiments and Results: *Ex Situ* Denitrification Scale-up Tests. The biotreatability of ground water was first investigated in batch experiments in 160 mL closed serum bottles. The ground water was collected from a single well located at the Tri-Tech site in Albuquerque's South Valley. The required amount of sodium acetate was determined using equations (1) and (2). In practice, sodium acetate was added to provide a C/N ratio of 1.42–2.00. Sodium trimetaphosphate (TMP) was added to give a concentration of 15–20 mg/l. Further scale-up tests were performed in a 208 L (55-gallon) drum and a 4542 L (1200-gallon) tank using the same carbon substrate and phosphorus nutrient. Reaction times for complete nitrate removal ranged from 7–15 days as shown in Table 7-1.

Table 7-1. Aboveground Denitrification Scale-Up Tests Using Indigenous Ground Water Bacteria (acetate used as carbon substrate, TMP as phosphorus nutrient)

Reactor Type	Volume (L)	Scale Ratio	Total Nitrogen (mg/l)	Time (days)	Denitrification Efficiency(%)
			Initial // Final		
Serum Bottle	0.12	1	99.4 // <0.1	7	100
Drum	200	1,667	101.6 // 1.1	7	99
Tank	4200	35,000	115.5 // <0.1	15	100

***In Situ* Denitrification Field Test:** The schematic diagram for the push-pull *in situ* field test is illustrated in Figure 7-1. The test was designed to keep the reacting ground water between the two monitoring wells. About 4200 L of contaminated ground water was pumped out from an extraction well and mixed with sodium acetate and TMP in a mixing tank. A bromide tracer was used to follow dilution of the reacting ground water. The amended ground water with bromide as a tracer was recharged into the injection well at a flow rate of 6 L/min. The ground water from injection and monitoring wells was sampled on a daily basis during denitrification. The post-sampling was carried out every 15 days over a period of two months. The ground water parameters of pH, conductivity, total dissolved solids (TDS), dissolved oxygen (DO), and Eh were measured in the field by a YSI 6920 water quality monitor installed in the flow cell as shown in Figure 7-5. Water samples were measured in the lab using a Dionex DX 500 chromatography system for anions: acetate, nitrate, nitrite, and sulfate. The concentration of bromide was measured using an ATI Orion Model 9635 *ionPlus* Series Bromide Electrode.

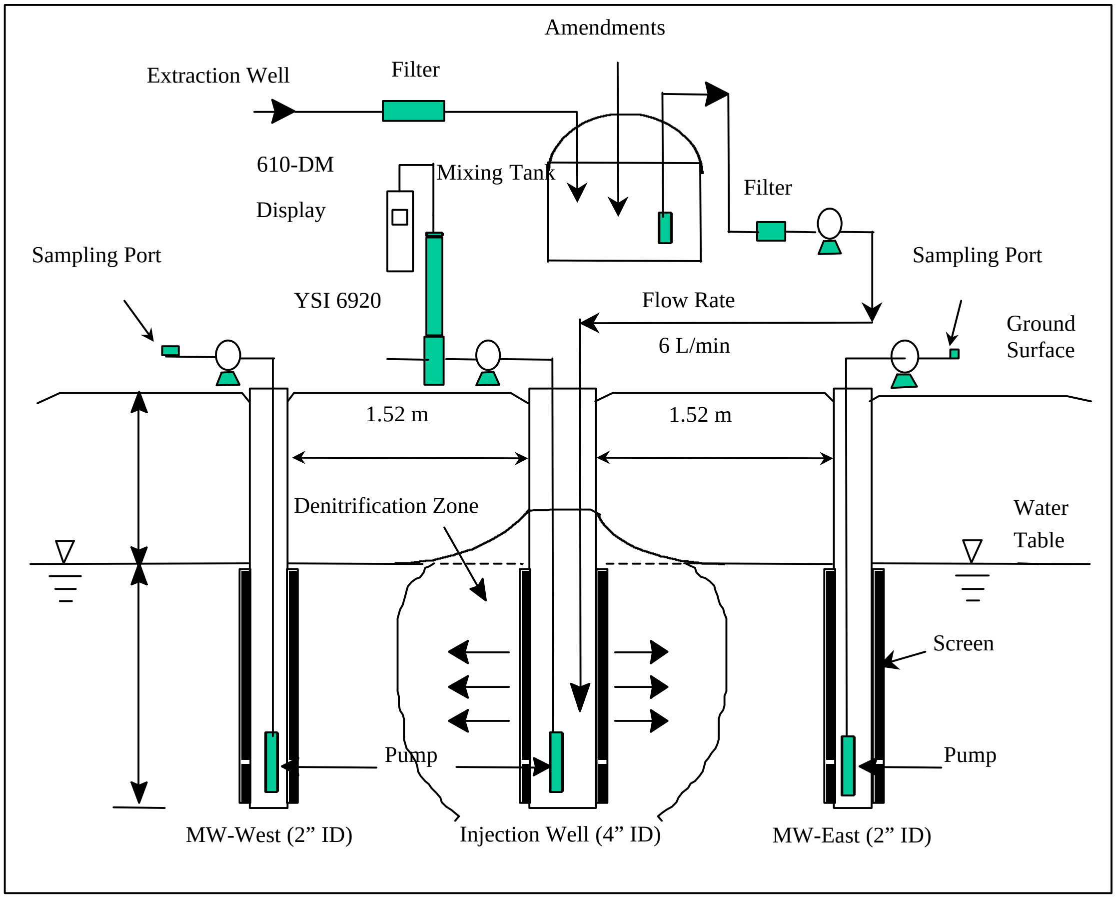

Figure 7-1. Design of an *In Situ* Denitrification Test at Tri-Tech Site, Albuquerque's South Valley (not drawn to scale)

Figure 7-2 shows the concentrations of acetate, nitrate, and nitrite versus time for samples taken from the injection well during denitrification. All traces of both nitrate and nitrite intermediate were removed in five days. The nitrate was metabolically transformed to nitrogen gas, and the final concentration was less than 1 mg/l.

Table 7-2 shows a comparison of average denitrification rates for three different process scales indicating that *in situ* average denitrification is nearly three times the average rate of *ex situ* tests. The faster *in situ* denitrification is likely due to the significantly greater bacterial concentration in the aquifer matrix as compared to the bacteria concentrations in water samples.

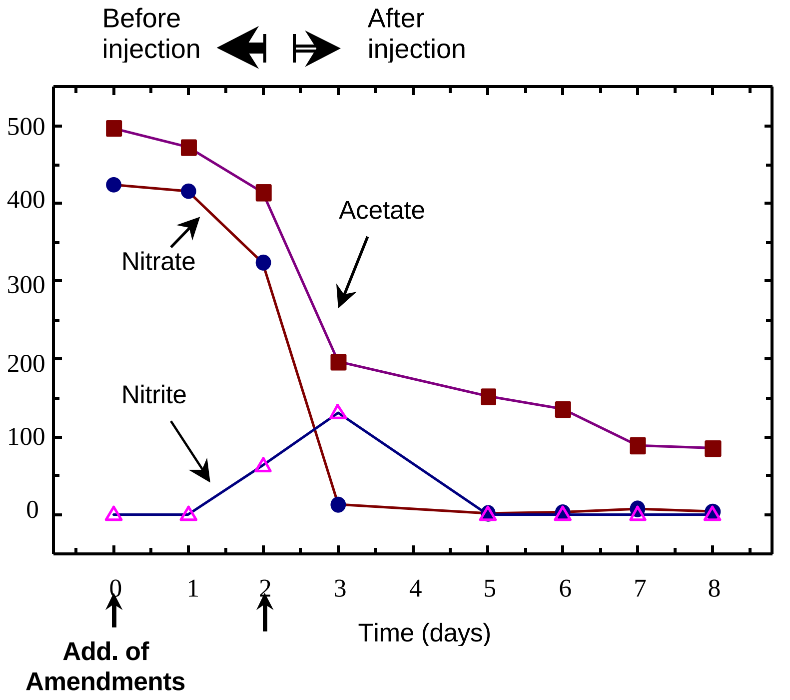

Figure 7-2. Reaction Concentration Curves Resulting from Short-Term Monitoring During an *In Situ* Denitrification Test

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Table 7-2. Comparison of Average Denitrification Rates Using Acetate and TMP as Amendments

Experiments	Temperature (^{o}C)	Denitrification Time (days)	Average Denitrification Rate (mg N /L/day)
Serum bottle test w/o sand	25	18	5.4
1200 gal tank test	20	15	6.9
In situ field test	20	5	19.0

Figure 7-3 shows the concentrations of acetate, nitrate, nitrite, and bromide versus time for water samples from the injection well over the two-month monitoring period. After the initial denitrification reaction was completed, the excess acetate was eventually consumed by further denitrification resulting from mixing of the surrounding contaminated ground water. This was confirmed by the decrease in bromide tracer. During the second reaction period, the nitrate concentration remained low until all the excess acetate was consumed.

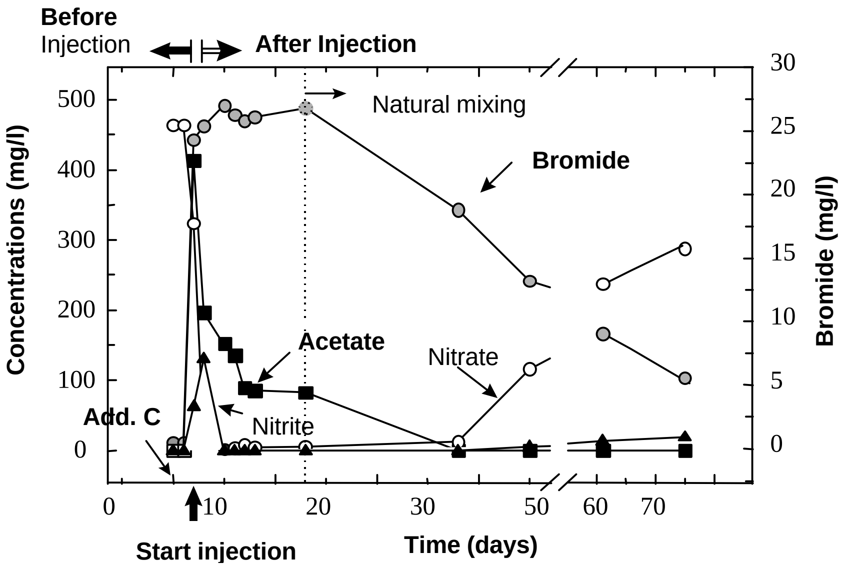

Figure 7-3. Reaction Concentration Curves Measured During an *In Situ* Biodenitrification Test

The long-term monitoring of ground water parameters of Eh, pH, conductivity, and dissolved oxygen were documented in Deng, 1998. Results also indicated that the Eh, pH, and conductivity values returned to background levels following the push-pull field demonstration.

As a continuation of this successful batch field test, a small-scale continuous field test was completed in April and May 1999 (see Figure 7-4). The results were similar to those from the batch experiment.

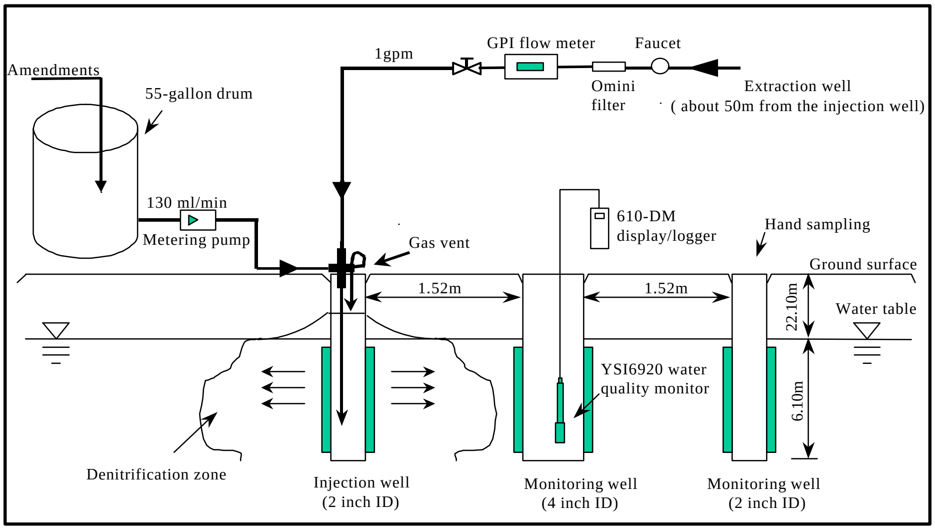

Figure 7-4. Modified Schematic Diagram of Continuous Denitrification Field Ttest

Figure 7-5 shows the decrease in nitrate concentration with time. The final concentration in the 4" monitoring well was near zero. During the experiment, some typical equipment deployment problems were encountered and solved. We also observed some biofouling. This topic is under investigation but is a common observation with *in situ* bioremediation processes. Well treatment procedures for biofouling are reported in the literature. The small-scale continuous test was successful, and now plans are underway for a larger scale continuous field test on the same plume but at a location closer to the heart or highest nitrate concentration location. A series of inverted 5-spot patterns are planned.

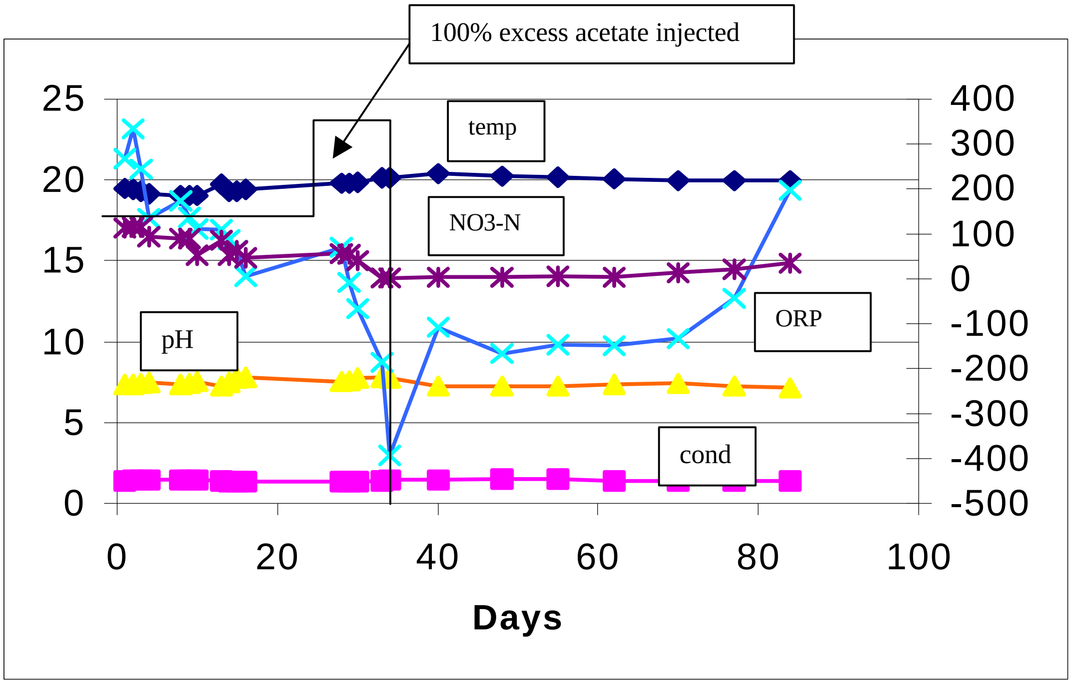

Figure 7-5. Denitrification Results from 4-Inch Monitoring Well Using YSI6920 Water Quality Monitor

Conclusions: *In situ* field denitrification performed very well resulting in complete nitrate removal and conversion to harmless nitrogen gas in less than five days. The approach of scaling-up the process in steps was very useful to confirm reaction rates and to show that reactor size is not important as long as there is good mixing of the amendments with the ground water. Because of the positive results, a larger scale continuous *in situ* demonstration is planned. The upcoming continuous *in situ* tests will evaluate costs, operation parameters/design, and address the issue of potential biofouling. Though the overall costs for *in situ* biodenitrification of ground water is still being assessed, our evaluation indicates that the amendment (sodium acetate and trimetaphosphate) costs will be about $0.64 per 1000 gal of ground water containing 20 mg/l nitrate-nitrogen and 4 mg/l DO. Due to the success to date of EISBD, UNM has recently licensed this technology to Key Technologies, Inc. of Albuquerque, New Mexico (Dr. Alan Kuhn, President).

7.2 UNL Professor Roy Spalding

Ground water denitrification research projects occurred on a private farmstead located about 3 km north of Central City in Merrick County, Nebraska. The site is centrally located in a county that is in the central Platte region of Nebraska. Merrick County has the dubious reputation of having the state's largest area underlain by nonpoint nitrate-nitrogen concentrations exceeding the MCL. The aquifer thickness is approximately 40 feet and nitrate-nitrogen concentrations are uniform with depth. Average concentration in the saturated fluvial sands and gravels was 40 mg/l NO_3-N L^{-1}. The water table lies about 2 m beneath the site and varies about 0.5 m seasonally. This site was considered an excellent choice for a denitrification field trial for the following reasons: (1) a willingness on the part of the landowner to allow us to use about 0.11 hectares of easily accessible property, (2) high and steady nitrate levels, (3) a relatively homogeneous aquifer matrix, and (4) a short distance to ground water.

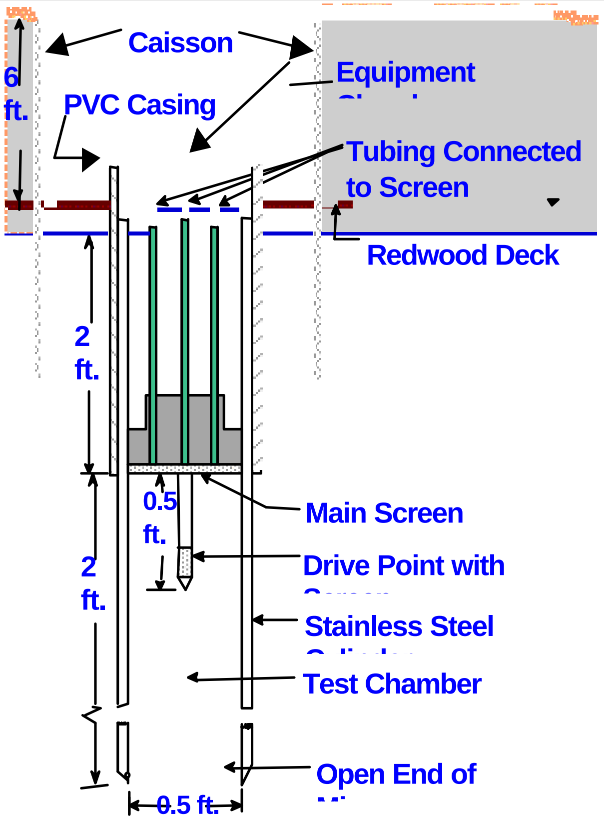

Figure 7-6. Cross-Sectional View of Subsurface Entry Caisson, *In Situ* Microcosm, and Multilevel Samplers (not drawn to scale)

To improve our understanding of the potential for denitrification at the site, access to the shallow aquifer was accomplished by excavating holes and inserting 2.5-m-long X 1.2-m-diameter caissons to depths slightly above the water table (Figure 7-6). A 0.25 m PVC casing was then inserted 0.61 m into the sediments, and the sediments were then removed by hand. A prefabricated stainless steel microcosm was then pushed into the aquifer (Bates and Spalding, 1998). Since the microcosms are open on the bottom, they become filled with aquifer material and ground water. When filled, each microcosm contains about 11 L, of which approximately 3.7 L are ground water.

Several experiments were completed over three years to determine the potential for denitrification. In each experiment, ground water in the microcosms was removed, amended with ethanol and bromide, and returned to the microcosm. The process is accomplished by drawing water into 10 L glass bottles from the microcosm through flexible tubing clamped on stainless steal tubes welded to the top of the microcosm. The retrieved water is amended with the above solutions via injection into the bottle, mixed, and pressure injected back into the microcosm through the screen. During this process, untreated water in the microcosm was displaced by the amended water and flushed through the open bottom out into the formation. The treated water was then monitored by collecting aliquots in 60 ml plastic syringes as the reaction proceeded. Nitrate, nitrite, bromide, bicarbonate, sulfate, chloride, dissolved oxygen, dissolved organic carbon, and the $\delta^{15}N$ values of the nitrate were routinely analyzed.

The results (Figure 7-7) using the ratio of C/N (1.25) are shown in the following generic equation for denitrification:

$$5C + 4NO_3^- + 2H_2O \rightarrow 2N_2 + 4HCO_3^- + CO_2$$

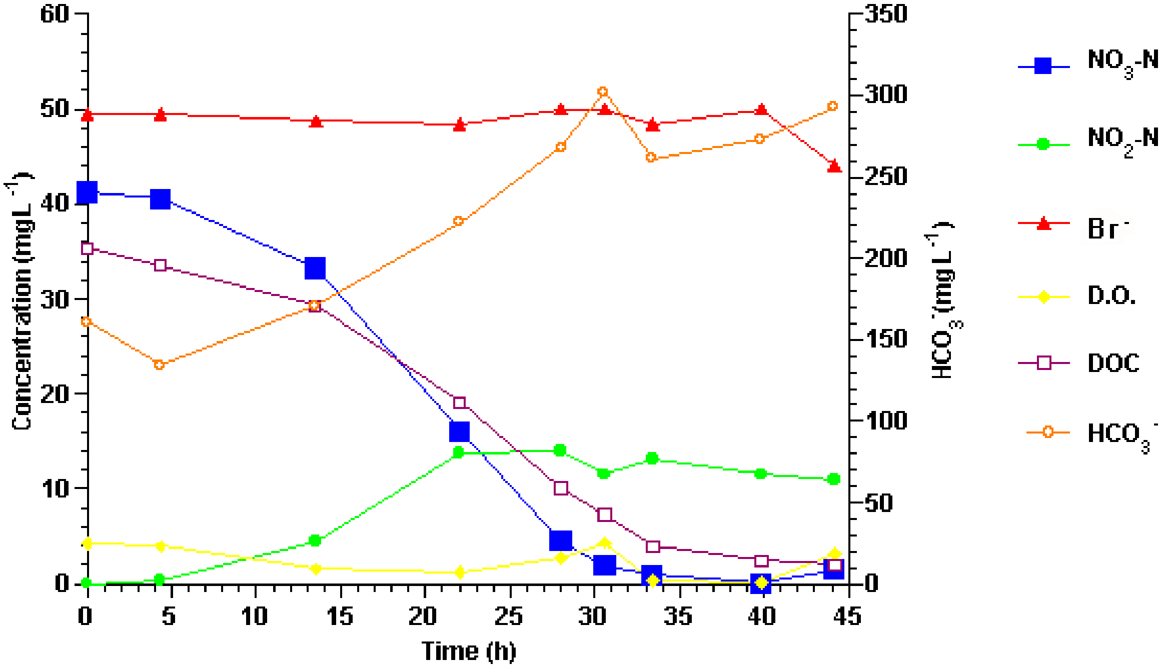

Figure 7-7. Concentration vs. Time for Selected Analytes Involved in or Affected by Microbial Denitrification in a Microcosm Amended with 50-mg C L^{-1}

In general, denitrification was stimulated after ~10 hours (h) when the DO levels were lowered to about 2 mg L^{-1}. Afterwards, the nitrate levels declined to nondetectable levels in about 20 h. As predicted in equation 1, bicarbonate concentrations increased dramatically (~150 mg L^{-1}).

The slopes representing carbon dioxide respiration versus residual nitrate plus nitrite averaged close to -1 at -0.88. This suggests that a small but significant portion of the carbon was assimilated by the bacteria to produce biomass. In the following equation, biomass production is shown to clarify the estimated incorporation of C and N by the bacteria.

$$97NO_3 + 50C_2H_5OH \rightarrow 5C_2H_7NO_2 + 75CO_2 + 84H_2O + 46N_2 + 97OH^-$$

(McCarty et al., 1969). Residual nitrite-N concentrations in these experiments increased to 10 mg L^{-1} and persisted after the termination in reduction at 40 h. In these experiments, denitrification (nitrate reduction to nitrogen), by the stepwise enzymatic process in which $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$, was incomplete, and nitrite remained at the termination of the reaction. The background level of DOC at 40 h suggested that there was insufficient available carbon to sustain the reduction to completion. The enzymatic reduction of nitrite is rate controlling in denitrification because it takes longer for some species of heterotrophic bacteria to synthesize nitrite reductase than the other reductases.

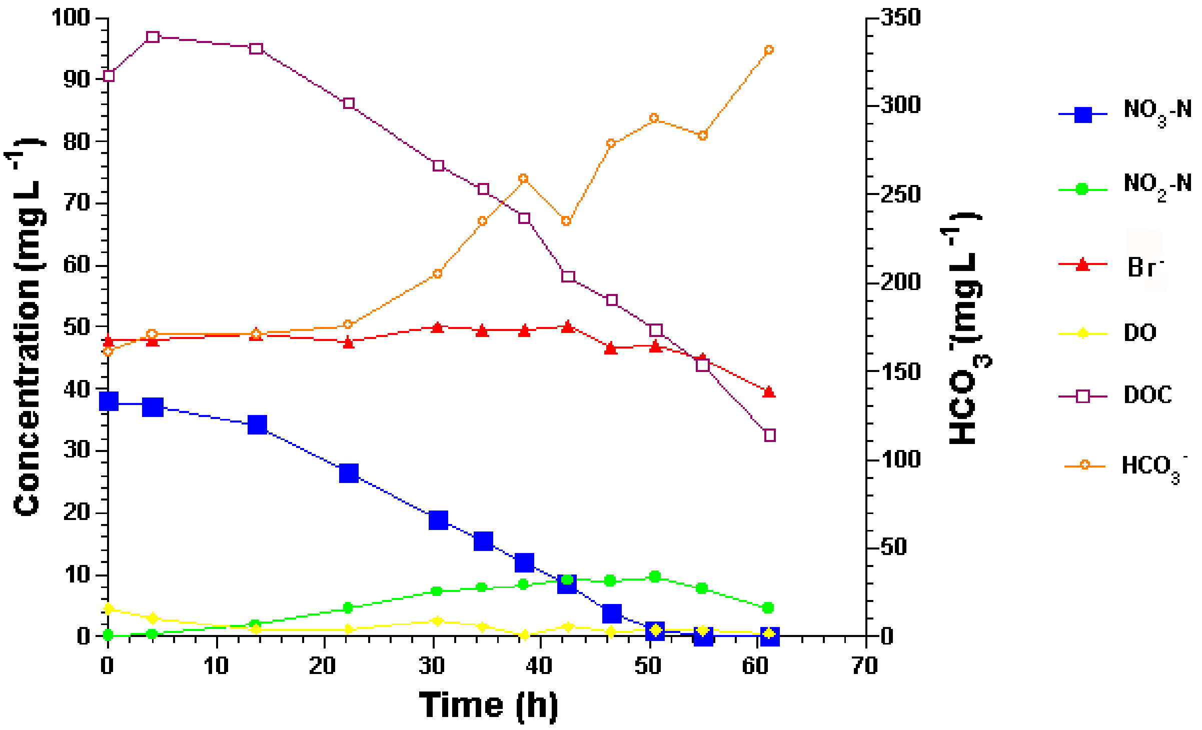

Figure 7-8. Concentration vs. Time for Selected Analytes Involved in or Affected by Microbial Denitrification Following Injection in a Microcosm Amended with 100 mg C L^{-1}

Thus, the following experiment was designed to promote complete denitrification by combining excess C with a more protracted monitoring period. In later experiments with excess carbon, the nitrite disappeared and complete denitrification occurred in 60 h. Using 100 mg C L^{-1}, a residual

C level of 38 mg L^{-1}, which is about ten times the background, remained at the termination of the reaction. This confirmed that the initial reaction (50 mg C L^{-1}) was at least 12 mg C L^{-1} deficient in available C.

Nitrate-nitrogen loss rates during amended denitrification experiments ranged from 18 to 32 mg L^{-1} d^{-1}. Rates were dependent on temperature and the amount of amended carbon. Cooler ground water temperatures apparently slowed the reaction as did excess available C. The $\delta^{15}N$ values of nitrate and nitrite are defined by the following equation and determined by isotope mass spectrometry.

$$d^{15}N\,(‰) = \frac{(^{15}N/^{14}N)_{\text{sample}} - (^{15}N/^{14}N)_{\text{standard}}}{(^{15}N/^{14}N)_{\text{standard}}} \text{ x } 1000$$

For many years, $\delta^{15}N$ values of nitrate have been pivotal in determining the sources of nitrate in many ground waters; however, their utility in determining ground water denitrification zones within the aquifer is somewhat of an emerging science. The application to the *in situ* microcosm permitted a very clear picture of the evolution of enriched $\delta^{15}N$ values during the denitrification process. As the reduction progressed, the $\delta^{15}N$ values increased from +6‰ to > +20‰ in the residual nitrate plus nitrite. By chromatographically separating the nitrate from the nitrite, the isotopic contribution of each species was determined (Bates et al., 1998). The experiments indicated that the presence of nitrite resulted in decreased $\delta^{15}N$ values for nitrate-N plus nitrite-N. When almost all nitrate and nitrite was denitrified near the completion of the reaction, the $\delta^{15}N$ values were close to +40‰.

The *in situ* microcosm data indicated that the nitrate-contaminated ground water could be remediated within days by the endemic aquifer bacteria without generating any hazardous by-products. Thus, the microcosm results support the application of amended denitrification as a treatment technology for nitrate-contaminated ground water. As an emerging technology, *in situ* denitrification has several advantages over the common aboveground methods, such as ionic exchange and reverse osmosis. Both methods are nontarget analyte specific and, thus, generate large amounts of wastes that are considered hazardous. As such, these wastes must be disposed of in specially operated secure landfills. These aboveground treatments are also expensive because they require large initial capital construction outlays, as do aboveground denitrification plants. *In situ* is economically and environmentally most attractive because it requires only a modest initial capital outlay, generates no hazardous waste, and is relatively economical to maintain and operate.

Two distinctly different *in situ* denitrification procedures were studied at the site in partial fulfillment of Imtiyaz A. Khan's Ph.D. In the first procedure, denitrification was promoted at shallower depths by injecting water containing known amounts of potassium chloride (KCl), bromide (Br), and ethanol near the surface of ground water perpendicular to the natural ground water flow. The injection line was 40 feet long and consisted of a ¾-inch-diameter perforated polyvinyl chloride (PVC) pipe, which was placed in a 50-foot-long trench to the water table depth of 7.5 feet. The reduction of nitrate was monitored by three fences of multilevel samplers (MLS) placed at 20, 40 and 60 feet downgradient from the injection line and vertically screened at 2-foot intervals. A premixed concentrate of KCl-Br solution and ethanol solution were metered into the injection line to yield a final concentration of 500 ppm KCl, 10 ppm Br, and 200 ppm-C in the injection water.

The injectate was chilled to 7°C by circulating it through a refrigeration unit. KCl injection and chilling were designed to increase the injectate density (ρ = 1.0008 gm/ml with total dissolved solid concentration of 900 mg/l) above that of ambient ground water (ρ = 0.99989 gm/ml with total dissolved solid concentration of 400 mg/l). This provided the necessary density gradient and promoted downward transport of injectate in the aquifer. The results indicated that complete denitrification occurred in a 60 ft X 40 ft area downgradient from the injection main and treated the aquifer water to a depth of 20 feet.

Clogging of the infiltration area surrounding the injection main was observed after 14 days of operation. The continuous presence of high concentrations of ethanol and nitrate near the injection main promoted an excessive growth of biomass and resulted in well clogging. Clogging is the nemesis of *in situ* denitrification and causes deleterious operational problems. To control clogging, subsequent experiments employed pulsed injection of carbon in nitrate free water. The pulsing technique described later alleviated the proliferation of biomass near the perforated main without affecting the performance of the process.

The second set of experiments were directed at nitrate remediation in the deeper portions of the aquifer and required the installation of a daisy well system (Khan and Spalding, 1998; Figure 7-9). The saturated sand and gravels have a thickness of about 40 feet and an average hydraulic conductivity of 250 feet/day. The daisy system creates a radial pattern of enhanced water levels at the injection wells, which are located along an outer circumference equidistant from a centrally located extraction well. When operating, the water table assumes a three-dimensional pattern similar to that described by a daisy flower.

The basic design consists of eight 4-inch-diameter outer perimeter wells, eight 2-inch-diameter inner perimeter wells, and a 6-inch-diameter centrally located extraction well (Figure 7-10). The outer and inner perimeter wells were located at a radial distance of 40 feet and 20 feet, respectively, from the extraction well. The outer perimeter wells were used to inject organic carbon (ethanol or acetate), thereby, creating a reducing zone in the segment between outer and inner perimeter wells. In this zone, most of the nitrate reduction takes place. The inner perimeter wells were used to inject an oxidant (hydrogen peroxide), which created an oxidized zone in the segment between the inner wells and the extraction well. In this zone, residual organic carbon, any residual nitrite, and bacterial by-products are oxidized before the denitrified water is removed from the aquifer.

All the wells were screened in the bottom 10 feet of the aquifer from 38 to 48 feet beneath the land surface (Figure 7-5). The injection wells were equipped with dipole packers for pressure injection and for circulation of the cleaning solutions into the aquifer matrix adjacent to the slotted intervals. The multilevel samplers were used to monitor the progress of the reaction and the two dimensional extent of denitrification.

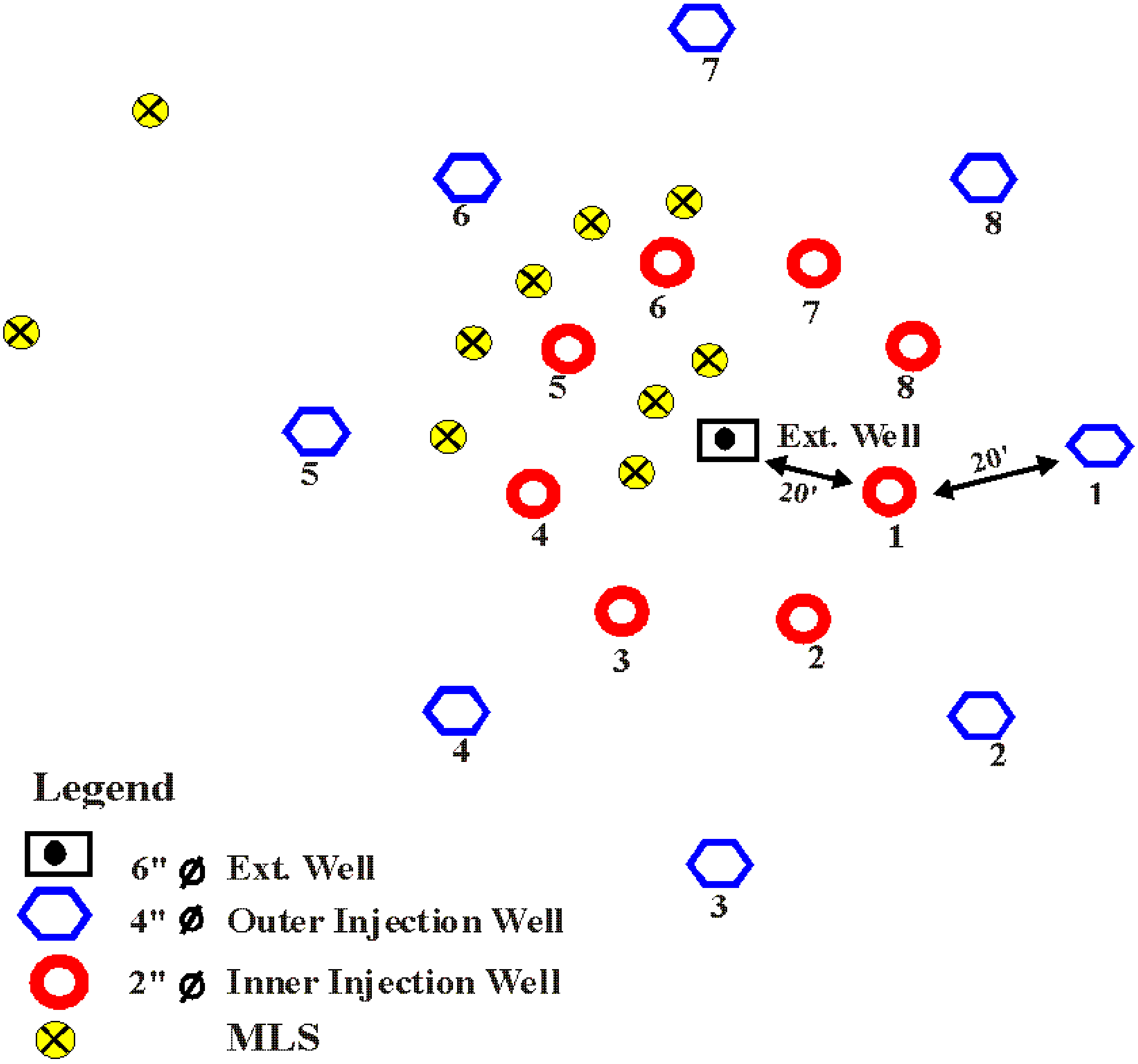

Figure 7-9. Layout of Daisy Injection System

In the preliminary investigation, the concentrated carbon source (ethanol) was injected directly into the nitrate-contaminated water to form a solution with 50 mg C L, and the solution was continuously injected into the aquifer at a rate of 37.8 L per minute. The extraction well was operated continuously at a rate of 151.2 L per minute to create an induced gradient towards the center of the daisy system. The results indicated successful denitrification of the 40 mg NO_3-N L ground water in multilevel samplers, located in the zones of denitrification without noticeable nitrite formation. However, there was a loss in specific capacity of the injection well due to accumulations of biomass at the screen and adjacent formation. Although the specific capacity of the injection well was restored with the dipole cleaning technique, it could not be sustained.

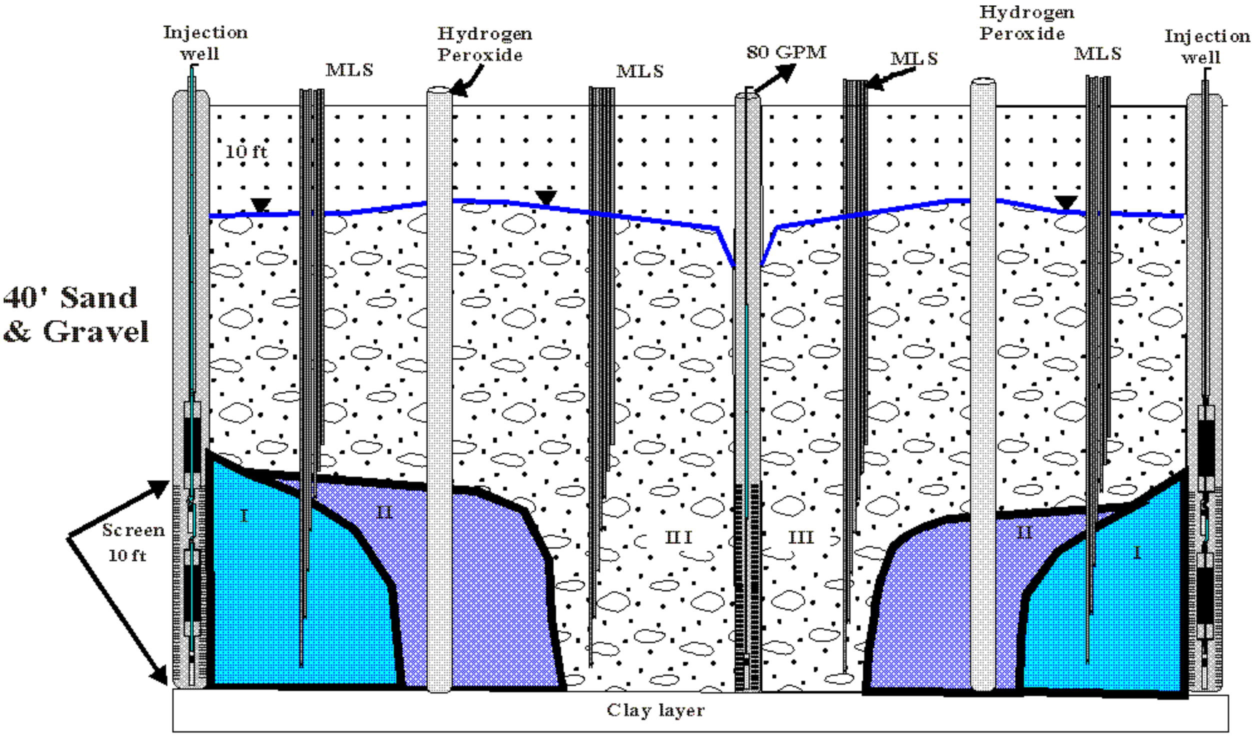

Figure 7-10. Vertical Section of Daisy Injection System. (I Reducing Zone, II Oxidizing Zone, III Treated Water Zone)

To prevent the injection well from clogging, a pulsing technique was developed using four outer perimeter wells. The basic approach of this methodology is to alternately pulse the injection of nitrate (electron acceptor), contaminated water, and ethanol (electron donor) into the aquifer. Pulsing requires nitrate-free water, which came from an onsite deep (140 ft) bedrock well tapping a five-foot thick limestone lens, to mix the 500 ppm C ethanol pulse. Simultaneous computerized injections were performed in a 6-hour cycle in opposite well pairs and then moved to the next well pair. Thus two injection cycles were completed every 24 hours. Each 6-hour cycle was composed of the following sequence of injections: (1) nitrate-free water for 25 minutes, (2) 500 ppm C L ethanol pulse for 40 minutes, (3) nitrate-free water for 25 minutes, and (4) 40 mg N/L nitrate-contaminated water for 4.5 hours. Each well rested for 6 hours between cycles. The results indicated that denitrification was complete in the impacted zones with no nitrite remaining after 9 hours (Figure 7-11).

The system remained free of detectable clogging during the three-week period. Approximately a 35% reduction in nitrate-N occurred at the extraction well (Figure 7-12). This reduction was in line with the treatment applied only to the bottom quarter of the aquifer from four of eight injection wells.

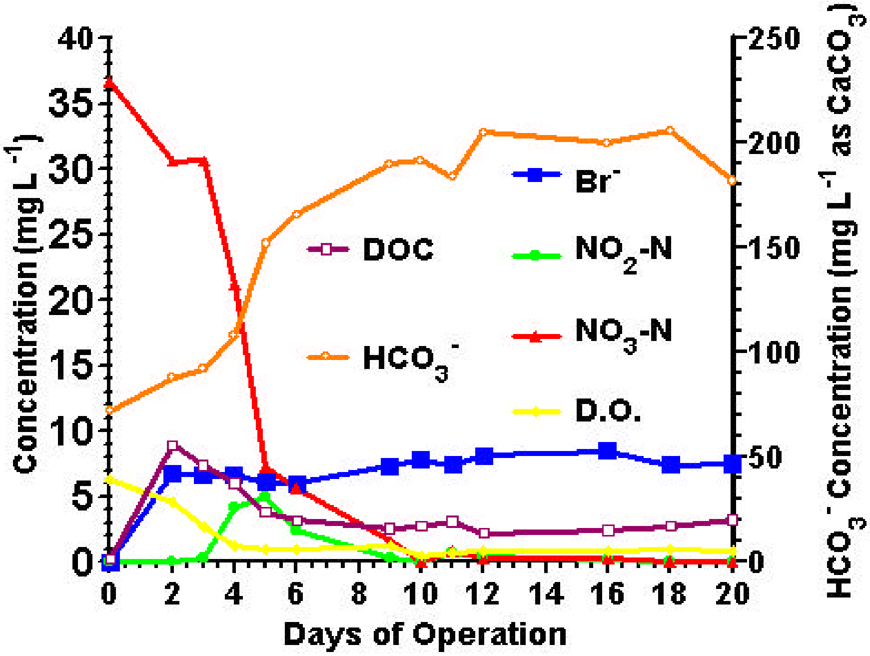

Figure 7-11. Anion, D.O.C. and D.O. Concentration in Inner Well #3. Complete Reduction Occurs in the Observation Wells Located in the Impacted Zones.

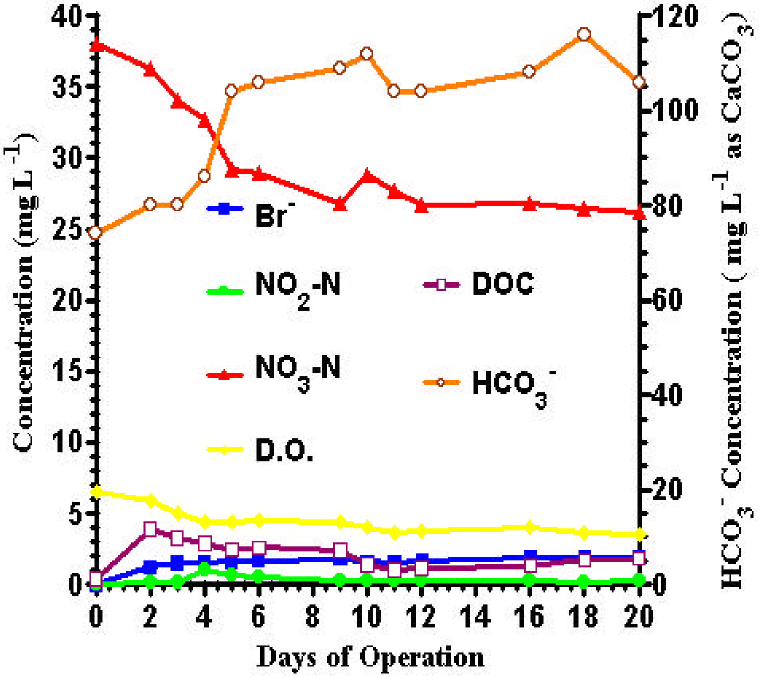

Figure 7-12. Anion, D.O.C., and D.O. under Pulse Injection in Extraction Well. 35% Nitrate is Reduced in the Capture Zone.

Sulfate reduction occurred in the most impacted aquifer zones. This may have resulted from excess ethanol significantly lowering the redox potential and promoting an unwanted bacterial side reaction. Detection of a hydrogen sulfide odor in the extracted water further confirmed sulfate reduction. To prevent undesired sulfate reduction, ethanol was replaced by acetate as the carbon source in the next experiment because acetate does not easily ferment and contains carbons with a higher oxidation state (“0”), than those in ethanol, which are at “-2”.

A three-month study was conducted to investigate the benefits of using acetate as a carbon source. The extraction well continuously operated at a rate of 151.2 L per minute. The experimental setup of the daisy system was the same as described earlier except only one injection cycle of a 6-hour duration was performed simultaneously in the two wells located opposite each other. All eight outer perimeter wells were used to inject acetate in a cyclic fashion, and periodically 0.1% hydrogen peroxide injections were made in the inner wells to prevent biofouling of the extraction well and oxidize any residual nitrite and hydrogen sulfide. Again, complete denitrification occurred in the entire perimeter area surrounding the extraction well throughout the 10-foot injection zone. No evidence of injection well clogging was observed. Residual dissolved organic carbon remained at background levels, and the maximum nitrite concentration observed was 0.2 mg-N/L, well below the maximum contaminant level (1 mg-N/L). A 45% reduction of nitrate occurred at the extraction well (Figure 7-7) without noticeable sulfide odor or loss of sulfate.

8.0 REGULATORY ISSUES

As previously stated in this document, nitrate contamination is pervasive, and regulatory enforcement of nitrate plumes has been limited. This section describes regulatory issues related to nitrate contamination and further identifies and describes regulatory issues specific to EISBD.

Appendix B contains a table of ground water standards for nitrate-nitrogen by state.

8.1 Regulatory Enforcement of Nitrate Contamination

Most state regulatory agencies have a difficult time dealing with nitrate-contaminated ground water. State pollution prevention programs are aggressively pursuing “permitting” to prevent further nitrate contamination in ground water. However, once a site becomes contaminated with nitrates above standards, especially nonpermitted facilities, the application of remediation practices to deal with nitrate contamination is lacking. There are various reasons for these phenomena.

8.1.1 Perceived Threat of Nitrate Contamination

Because nitrate-contaminated ground water’s only proven health affect, methemoglobinemia, is not perceived as a grave health threat compared to contamination by volatile organic compounds or certain metals, nitrate is not treated as a contaminant of highest concern. It should be emphasized that even if the previous statement is correct, the nitrate standard of 10 mg/l $N0_3$-N must be enforced according to federal and most state standards. Since the most common solution to nitrate contamination is to provide an alternate water supply, many regulators view the problem as resolved once this is accomplished. This does not deal with the nitrate plume that may persist, creating further problems in the future.

8.1.2 No Real Economic Remediation Technology

While pumping nitrate-contaminated ground water and disposing of it in some fashion is the simplest remediation technology, nitrate in ground water can be dealt with by means of treatment, such as reverse osmosis or ion exchange. However, the high cost and time involved in these efforts is a strong deterrence for regulators to require remediation.

Furthermore, most parties responsible for causing nitrate contamination do not have deep pockets. Examples of this would be small population centers that have wastewater treatment systems that are improperly constructed or managed and small, privately owned animal operations. These “mom and pop” operations do not have the financial resources to support a long-term pumping remediation system. Those responsible parties that do have greater financial capabilities rarely pursue nitrate remediation on their own—often because of the low perception of threat mentioned above.

Many nitrate-contaminated ground water sites are the result of nonpoint sources. Examples of this would be areas in the Midwest where agricultural land has been over fertilized consistently, but no one field is the sole source of the nitrate contamination. Housing developments with septic tank leach-field treatment systems have also caused regional nonpoint source nitrate contamination. When this occurs, there is no single responsible party for regulators to pursue to require remediation. This leaves many states with contaminated ground water and no allocated or available resources for remediation.

8.1.3 No Voluntary Plume Remediation

Many states have regulations or are in the process of developing regulations that allow responsible parties to voluntarily remediate ground water contamination. These regulations are fairly recent and provide incentives for responsible parties to adequately deal with their environmental concerns. Prior to these regulations, most responsible parties rarely initiated cleanup of their problems unless there was some direct benefit. Again, since nitrate is not a contaminant of highest concern, voluntary remediation of nitrate contamination was unheard of and unexpected. However, with these new voluntary remediation regulations, the situation may change.

8.1.4 Non-RCRA or CERCLA Constituent

Since nitrate is not a Resource Conservation Recovery Act (RCRA) or Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) constituent, these federal regulations have not applied to nitrate contamination. Those facilities that fall under RCRA and CERCLA regulations have not been required to deal with nitrate contamination. Only when nitro-aromatic contaminants have been present have RCRA or CERCLA facilities dealt with nitrate contamination. However, the situation may be changing with the new understanding and remediation technology of natural attenuation and the need for an electron acceptor. Nitrates act as an electron acceptor under certain conditions, and nitrate contamination might be addressed through natural attenuation of volatile organic compounds. DOE and DOD have shown an interest in dealing with nitrate contamination at some facilities and are very much interested in EISBD.

8.1.5 Impacts to Public and Domestic Supply Wells

A nationwide survey by EPA in the late 1980s gives a general indication of the extent of nitrate impact on public and domestic supply wells (EPA, 1992). These estimates are as follows:

- Approximately 30,300,000 people drink ground water from about 9,900,000 domestic wells in the United States. About 450,000 of these individuals are infants under the age of one year.
- Approximately 136,000,000 people drink ground water from about 94,600 public water supply wells nationally. About 2,000,000 of these individuals are infants under the age of one year.
- Of the population that obtains drinking water from domestic wells, approximately 1,510,000 are estimated to be consuming water with at least 10 mg/l nitrate-nitrogen. Of the people exposed at this level, about 22,500 are estimated to be infants younger than one year and thus possibly at risk of developing methemoglobinemia.
- Of the population that obtains drinking water from community water supply wells, approximately 2,980,000 individuals are estimated to be consuming water with at least 10 mg/l nitrate-nitrogen. Of these, about 43,500 are expected to be infants.

Even though the above statistics show a considerable impact of nitrate on public water supplies, federal and state regulations are designed to help ensure that public supply wells meet standards. As these figures indicate, nitrate contamination has probably impacted more public supply wells than any other contaminant. Usually treatment occurs at the wellhead, or a new public supply of water is provided. In many cases, regulators are quick to identify and rectify nitrate contamination at public supply wellheads.

Many states do not have any regulatory standards for domestic supply wells. In New Mexico alone, more than 700 documented domestic supply wells have been impacted with nitrate contamination above standards. For those states that have ground water standards for nitrate, regulations may be in place to address the nitrate contamination. Unfortunately, as previously mentioned, little can be accomplished to deal with the nitrate plume except to provide a clean alternate water supply or make recommendations for the domestic well owner. These recommendations may include identification of the nitrate source, steps to prevent further nitrate contamination, and suggestions to deepen or move domestic wells beyond the nitrate contamination, if applicable.

8.2 Issues Specific to Enhanced *In Situ* Biodenitrification

8.2.1 Time of Cleanup

As shown in the data provided in Section 6.0, EISBD is a very fast reaction. To achieve contaminant removal to below standards or detection limits in a contaminated aquifer in an expeditious manner is highly desirable. Few regulations mandate how quickly a contaminant must be removed. Many specific site plans approved by regulators contain timeframes for contaminant removal. Most regulators would approve of a remediation technology that is faster. Regulators must be aware that for EISBD to be effective, the denitrification process must be completed to term. That is, nitrate must be reduced to nitrogen gas, or intermediate contaminants, such as nitrite, may be left. Therefore, the responsible party needs to assure that enough carbon and nutrient amendment is supplied in the aquifer over an appropriate time and at appropriate concentrations.

8.2.2 Not Yet a Proven Technology

Innovative technologies for environmental restoration promise faster, better, and cheaper remediation. Yet, institutional, regulatory, and technical barriers related to the use of innovative technologies often arise by virtue of (1) lack of cost and performance data and (2) an inflexible institutional/regulatory framework. These general issues are explained in detail in ITRC's *Case Studies of Regulatory Acceptance: In Situ Bioremediation Technologies.* Section 3.3.1 of this document is repeated below.

The risks associated with uncertain performance of innovative technologies include the following:

- Risk aversion. Regulators charged with assuring a safe and effective cleanup, may be unwilling to assume the risk of an innovative remedy that may not prove to be either safer or effective. Regulators must be accountable to both their management and the public when assuming these risks.

- Desire to expedite cleanup. Remedial site managers (i.e., regulators) must adhere to schedule milestones. Responsible parties benefit from getting the site out of the media, the public eye, and regulatory scrutiny. Public opinion generally favors immediate action. However, the initial delay associated with the study and testing of the innovative technology, coupled with the uncertainty of its performance and possible necessity for follow-up remediation, can give pause to those concerned with expeditious remediation.

- Desire to maintain a projected budget. Remedial site managers are under pressure to maintain projected budgets, and responsible parties have a significant incentive to minimize cleanup costs. Yet the study of an innovative technology may drive up costs in the short-term. If the technology should not perform as expected, budgets may be overrun.

Regulatory drivers also may impede the implementation of innovative technologies. Such regulatory concerns include the following:

- Regulatory standards. Frequently, regulatory standards can actually impede, rather than facilitate a cleanup. Examples include land disposal restrictions that prohibit removal of contaminated media, treatment, and land disposal if the media contains listed hazardous wastes. Ground water quality standards can inhibit injection of additives that accelerate the biodegradation of chemicals in ground water.

- Permitting procedures. Permitting of innovative technologies is often a lengthy process and a process that is unfamiliar to many regulators (e.g. Research, Development and Demonstration permits under the Resource Conservation Recovery Act). Additionally, there is potential for interagency friction when one agency is ready to approve use of an innovative technology, but another agency feels compelled to adhere to its established permitting process.

8.2.3 Long- and Short-Term Regulatory Issues

Long- and short-term regulatory issues deal primarily with monitoring requirements. It goes without saying that continued monitoring of ground water quality is required during EISBD. Most states require some type of permit for the injection of water. These permits have monitoring requirements. Short-term requirements are usually specified in detail in those permits. Since EISBD reactions are very fast, short-term ground water monitoring will verify the efficiency of denitrification. Long-term requirements after denitrification also vary between states. New Mexico requires that eight consecutive quarters of below standard ground water analysis be conducted prior to closure approval.

8.2.4 Reinjection of Contaminated Ground Water and Amendments

As with many enhanced bioremediation technologies, the same regulatory issues re-emerge. These issues are well explained, and solutions are provided in ITRC's *Technical and Regulatory Requirements for Enhanced In Situ Bioremediation of Chlorinated Solvents in Groundwater*, Appendix E. The following text was taken directly from that document.

"Regulatory Barriers Preventing Deployment of *In Situ* Bioremediation Technologies"

During the course of development of the *Regulatory and Technical Guidance for In Situ Bioremediation of Chlorinated Solvents in Groundwater*, the Enhanced *In Situ* Bioremediation Work Team identified a major regulatory impediment to the deployment of a particular class of *in situ* bioremediation. The critical elements of this technology include

- withdrawal of contaminated ground water,
- addition of amendments to the ground water, and
- injection of the contaminated ground water back into the contaminant plume without substantially reducing the concentration of contaminants in the injected fluid.

Withdrawal and injection results in the establishment of a recirculation cell that helps to distribute the amendments throughout the targeted plume and increases the residence time within the treatment zone. Once distributed within the ground water, the amendments stimulate microbial biodegradation processes that can significantly reduce the mass of contaminants.

This type of bioremediation system triggers the following RCRA-related regulatory issues:

- Withdrawn ground water may be considered a contaminated media under EPA's "contained-in" policy *(40 CFR 261.33(b)*).
- Withdrawal may constitute active management of hazardous waste, thus triggering land disposal restrictions *(RCRA Section 3004 (f), (g), and (m)*).

- Contaminated media is to be treated as hazardous waste until it no longer contains the listed hazardous waste. The Toxicity Characteristic (40 CFR 261.24, Table 1-1) concentrations have been used to determine the level above which ground water is to be treated as hazardous.
- Injection of hazardous waste into a usable aquifer constitutes land disposal *(RCRA Section 3004 (f), (g), and (m) and 3020(a))*. Because contaminated media under the "contained-in" policy requires treatment as hazardous waste, LDR restrictions could apply.

RCRA attempted to address the fourth issue by specifically allowing the reinjection of treated ground water for the purposes of remediation in the case of RCRA or CERCLA cleanups *(RCRA Section 3020(b))*. However, this statute has been interpreted to require substantial treatment resulting in reduction of contaminant levels prior to reinjection. Proponents of this technology maintain that it is often not economically feasible to clean up the contaminated ground water prior to reinjection and argue that there are no sound scientific or risk-based justifications for doing so. Furthermore, there appear to be no federal regulatory mechanisms to allow the reinjection to occur in non-RCRA or non-CERCLA sites.

The following issues should be addressed:

1. <u>Reinjection RCRA 3020(b)</u>

Issue: RCRA 3020(b) states that contaminated ground water must be treated to substantially reduce hazardous constituents prior to reinjection. It is unclear whether this requires both treatment *and* a reduction of contaminant levels prior to injection, or just substantial treatment prior to injection with the ultimate result being a reduction in contaminant levels within the aquifer.

Solution: Clarify this statute to allow treatment by nutrient addition or bioaugmentation that will constitute substantial treatment *in situ*.

2. <u>Non- RCRA or non-CERCLA contaminated sites</u>

Issue: If the site cleanup (regarding ground water and related contaminants in this situation) <u>is not</u> conducted under CERCLA or RCRA Corrective Action authority, then it is unclear whether CERCLA or RCRA regulatory mechanisms would apply to allow injection (such as RCRA 3020b).

<u>Solution</u>: Clarify that state remedial and voluntary cleanup programs should have the same regulatory mechanisms to expedite cleanups as CERCLA and RCRA Corrective Action unless more restrictive state regulations supercede the federal regulations.

3. <u>Area of Contamination or Corrective Action Management Unit</u>

Issue: A CERCLA–AOC (Area of Contamination, 40 CFR, part 300) or a RCRA–CAMU (Corrective Action Management Unit, 40 CFR, part 264, subpart S) were designed to facilitate rapid and cost-effective site remediation by reduced regulatory requirements as long as waste is managed (treated, stored or disposed) within the AOC or CAMU. If managed within the AOC or CAMU, Land Disposal Restrictions (LDRs) treatment standards and minimum technology requirements (MTRs) will not be triggered.

Solution: Clearly define that an AOC or CAMU can be defined by the aerial extent of the plume, thereby allowing aboveground extraction and reinjection (i.e., a recirculation system) without triggering LDR and MTR requirements.

4. OSWER Directive 9380.0-25, 4/29/96

Issue: EPA is encouraging the demonstration and use of promising new technologies, including those involving injection of amendments to enhance biodegradation (OSWER Directive 9380.0-25, April 29, 96.)

Solution: Clarify/modify this directive to clearly include the use of amendments added to extracted ground water to enhance *in situ* bioremediation.

5. Treatability Variance

Issue: When an AOC or CAMU approach cannot be used for any reason, it is unclear whether it would be appropriate to use a Treatability Variance (40 CFR 268.44) to establish ultimate cleanup levels. Can a Treatability Variance be obtained to allow extracted ground water to be reinjected into the subsurface to enhance *in situ* biotreatment technologies?

Solution: Clarify that Treatability Variances can be issued to promote the use of amended ground water injected into the aquifer to accelerate *in situ* bioremediation.

5. UIC Considerations

Issue: UIC wells: When extracted ground water is to be treated as hazardous waste under the "contained-in" policy, reinjection into a useable aquifer to enhance bioremediation could be considered a Class IV injection. This injection would be prohibited for most non-CERCLA or non-RCRA sites (40 CFR 144.13). This could force unnecessary treatment of amended ground water prior to reinjection and may result in unacceptable costs for EISB projects.

Solution: Clarify that wells being used for reinjection of amended ground water to enhance bioremediation may be classified as a Class V well rather than Class IV wells.

8.2.5 Residual Amendments

EISBD utilizes a substrate as a carbon source for bioremediation. The addition of a carbon source raises regulatory concerns. These concerns are based upon any carbon source that may remain following denitrification. Even if excess carbon is supplied to an aquifer, facultative bacteria will continue to consume this excess carbon until depleted, thereby removing any residual amendments. Regulators should be aware that further monitoring of the excess carbon source should take place if the carbon source amendment is a chemical of concern.

8.2.6 Resulting Geochemistry in Aquifer

Aquifer geochemistry may be altered from background after EISBD. Excess CO_2 and H_2O will be the end products of the added carbon source. The CO_2 most likely will increase bicarbonate levels in the aquifer. Since denitrification occurs in anaerobic conditions with a carbon source, other electron acceptors besides NO_3 may be MnO_2, FeO_3, $FE(OH)_3$, or SO_4. Evidence of manganese and iron reduction is expected to be seen but not sulfate reduction. The decreased values of Eh during EISBD are not low enough for sulfate reduction to occur. However, one should expect an increased dissolved concentration in Mn(II) and Fe(II). During EISBD, an increase in pH will occur, but subsurface environments probably will be able to buffer the pH. The decrease of pH after denitrification is most likely explained by the precipitation of certain cations, such as the precipitation of calcium carbonate or magnesium carbonate. Major sources of nitrate contamination are usually associated with an increase in TDS. After denitrification, TDS concentrations remain similar to TDS concentrations found in the nitrate plume.

8.2.7 Biomass Concentrations

The potential for biomass accumulation with any enhanced bioremediation is a regulatory concern. Biomass buildup may prevent even distribution of the carbon source and nutrient into the aquifer. Uneven distribution may not provide for complete denitrification. Biomass accumulation may occur in the well or amendment-distributing system, creating clogging and improper treatment or denitrification. The choice of amendment is critical for minimal assimilation of the carbon by the bacteria. As shown above, acetate is an amendment of choice since dissimulation occurs with acetate. Regulators should be aware that if bacterial accumulations are great in the aquifer, their biomass breakdown after completion of denitrification might release nitrogen back into the aquifer. However, this release of nitrogen will be slow, and concentrations may not exceed standards.

9.0 PERFORMANCE PARAMETERS

9.1 Cost

EISBD projects have costs related to chemical amendments and engineered amendment injection systems, well construction, system maintenance, and monitoring. Due to the limited availability of information on completed projects, little cost data is available. However, cost comparisons can be made between enhanced bioremediation and typical pump-and-treat systems. DuPont has developed a method of evaluating technologies that includes a generic, nonsite-specific basis using a template site. One such comparison was based on a chlorinated solvent site where enhanced bioremediation cost $1.20 per 3,780 L treated, versus a pump-and-treat cost of $8.90 per 3,780 L treated. (Quinton et al., 1997). Cost analysis can be presented for EISBD work completed or proposed at this time.

As noted under UNM's EISBD project, the cost for chemical amendments is $0.64 per 3,780 L treated, given concentrations of 20 mg/l nitrate-nitrogen and 4 mg/l dissolved oxygen. A proposal to remediate the heart of a nitrate plume in New Mexico with concentrations of approximately 300 mg/l nitrate-nitrogen should be ongoing. The proposal includes a two-year project to assess the center of plume mass, install and operate four inverted five-spot injection/extraction well patterns, and monitoring of ground water. Project cost estimates are approximately $106,000 per year. Since this is a joint project between the New Mexico Environment Department and UNM, many of the costs are associated with research. Research costs indicate a costlier estimate than if this technology were already commercialized.

In *ex situ* denitrification, the University of Colorado has shown that a complete denitrification system costs approximately $60 per 3,780 L treated (Silverstein, 1997).

9.2 Time to Completion

As described previously, EISBD is a very fast reaction, given the correct conditions. Reduction of nitrate to below detection limits can occur in a matter of days. Given this information, the time to complete a remediation of a nitrate plume would depend on site concentrations and conditions and regulatory requirements for closure monitoring. It is conceivable that a site could receive closure within six months but most likely would require two years. When EISBD is applied to remediate ground water before it is pumped into a supply well, the time to completion would be dependent on the size of the plume and the life of the supply well.

9.3 Contaminant Reduction

The denitrification work of both UNM and UNL showed that EISBD occurs in days, ranging from 5 days to 15 days. Contaminant reduction is very dependent on the initial nitrate concentration, the ability to disperse substrates evenly through the aquifer, and initial dissolved oxygen concentrations. In any event, denitrification occurs very rapidly. As compared to most treatment systems that require pumping of ground water, EISBD is considerably more desirable. The pumping of ground water to contain and remove nitrates takes years with considerable costs, regulatory oversight, maintenance, and monitoring.

10.0 PUBLIC AND STAKEHOLDER ACCEPTANCE AND CONCERNS

EISBD is an innovative technology that poses some public and stakeholder concerns. This document shall address concerns that are typical to all remediation technologies and concerns that are specific to EISBD.

Noise is a concern in any remediation technology implementation. During the initial stages of implementation of EISBD injection, extraction and monitoring wells need to be installed. Drilling activities may create noise hazards but are short-lived until well completion. During operation of EISBD projects, noise is very limited since pumping of ground water for amendment addition is the only mechanical process that may create noise.

Prior to initiation of drilling activities, access to properties overlying the nitrate plume have to be obtained. In urban settings, access may be a problem but is dependent on site conditions, public access, and private ownership of the site. During installation of an EISBD project, drilling vehicles will be mobilized and may cause temporary traffic concerns and dust. This concern too is short-lived. During the operation of EISBD projects, extraction wells require electrical pumps.

Pumping rates are dependent on site conditions such as ground water concentrations, amendment additions, and lithology. Pump houses and their exhaust systems may require sound and off-gas mitigation. The same holds for vibration from pump operations.

During active denitrification, nitrogen gas is produced but is innocuous, and the majority probably will remain in the soil vapor environment. EISBD principals involve the stimulation of indigenous bacteria to denitrify ground water, resulting in the proliferation of denitrifiers as they out compete other microorganisms. Therefore, pathogen proliferation would most likely be at a minimum and would pose very little concern. As with any emerging technology, uncertainties may occur. At least two technology uncertainties are foreseen at this point. One is the potential for biomass buildup that may cause biofouling in the injection wells or the saturated zone. Since this is the nemesis of any *in situ* bioremediation technology, this problem has been studied and solutions are available depending on site conditions. Timely communications with affected stakeholders on the biofouling testing timetable, results, and solutions are a must for maintaining trust. The second is the presence of ammonia. As previously stated, ammonia is a major source of nitrogen in fertilizers, explosives, and human and animal wastes. In the presence of oxygen, ammonia will easily convert to nitrate and, therefore, must be addressed along with the nitrate. Remediation technologies must address ammonia contamination along with nitrates.

Please refer to Section 8.2.4 concerning reinjection issues. However, since ground water is extracted and reinjected, water table issues may be of concern. The EISBD process is to extract nitrate-contaminated ground water, amend the extract with nutrients and a carbon source, and reinject to allow for *in situ* denitrification to occur. This will cause water mounding and drawdown, but the system is designed for hydraulic containment and should only pose minor concerns. Constant measurement near buildings with basements will ensure a level of comfort.

Overall, this technology is very cost-effective compared to all other remediation technologies. It is also very environmentally friendly because nontoxic amendments are used, water resources are not wasted or consumed, and residual products are innocuous. It must be pointed out that the EISBD process must be carried out to completion. That is, nitrates are denitrified to nitrites, and nitrates are denitrified completely to nitrogen gas. Otherwise if nitrites are left in the ground water, they will either be converted back to nitrates or may remain as nitrites, which is the contaminant that can cause the greatest human health risk. To assure that denitrification is carried out to completion, an ample supply of carbon source has to be present, and monitoring for the final conversion of nitrate to nitrogen gas must be provided to give assurance to the community that the process is complete.

11.0 CONCLUSIONS

With a growing population and its demands for quality drinking water, the need is urgent to protect and preserve ground and surface waters as limited natural resources. With potable water seen as a renewable resource, its protection, preservation and reuse must continue to be appropriately managed. One management tool being studied is the reinjection of potable water into an aquifer as a reservoir. This would be hindered if introduced into a nitrate ground water plume. Pollution prevention of nitrogen sources must continue to help alleviate further nitrate contamination in our drinking water supplies. A review of U.S. and foreign studies indicates a need for more peer review of health effects studies of nitrate contamination on humans and animals. For instance, the many links between the intake of nitrate-contaminated water and adverse health effects, such as miscarriages and cancers, need to be studied and evaluated. Due to high cost, long-term treatment, and relative ineffectiveness, traditional nitrate remediation techniques are limited. The application of new and emerging remediation technologies for nitrate contamination is promising. EISBD is one of the most promising emerging technologies to eliminate nitrate contamination. Current research and application of this new technology show that remediation costs and time are substantially reduced; it is efficient; its applicability is diverse; and regulatory, public, and commercial acceptance is imminent. Many federal facilities, including those owned by DOD and DOE, have ground water contamination. In some places, this contamination is solely composed of nitrates or other contaminants commingled with nitrates. EISBD may be implemented in association with other *in situ* bioremediation applications where these singular or commingled plumes exist. EISBD appears to be one of the most promising of the few emerging technologies to deal with nitrate-contaminated water.

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APPENDIX A

Acronyms

Acronyms

AOC	Area of Containment
CAMU	Corrective Action Management Unit
CDCP	Center for Disease Control and Prevention
CeRaM	Center for Radioactive Waste Management
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CT	carbon tetrachloride
DO	dissolved oxygen
DOC	dissolved organic carbon
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
ECOS	Environmental Council of States
EISBD	enhanced *in situ* biodenitrification
EPA	U.S. Environmental Protection Agency
ERIS	Environmental Research Institute of States
HMX	oxyhydro 1,3,5,7-tetranitro-1,3,5,7-triazine
ITRC	Interstate Technology and Regulatory Cooperation Work Group
KCl	potassium chloride
LDR	land disposal restrictions
LLC	limited liability corporation
MCL	maximum contaminant level
MLS	multilevel samplers
MTR	minimum technology requirement(s)
MOU	Memorandum of Understanding
OSWER	Office of Solid Waste and Emergency Response
PRB	permeable reactive barrier
PVC	polyvinyl chloride
RCRA	Resource Conservation Recovery Act
RDX	2,3,5-trinitro-1,3,5 triazine
SD	South Dakota
TDS	total dissolved solids
TMP	sodium trimetaphosphate
TNT	2,4,6 trinitrotoluene
UIC	underground injection control
UNL	University of Nebraska-Lincoln
UNM	University of New Mexico
WERC	Waste-management Education and Research Consortium
WI	Wisconsin

APPENDIX B

State Nitrate Ground Water Standards

Survey of Nitrate Ground Water (GW) Standards by State

All concentrations are measured as Nitrate - Nitrogen unless otherwise stated

State and Name	Standard	References
Alabama Fred Mason, (334) 271-7831	No current action level for cleanup	Have adopted risk-based methodologies for cleanup and have program specific permitting for gw protection. ASTM Subcommittee E 50.04, "Provisional Standard Guide for Risk-Based Corrective Action"
California Carl Hauge, (916) 327-8861	45 mg/L	Title 22, CA Code of Regulations, 64331 & 64444.
Delaware Ron Graeber, (302) 739-4761	10 mg/L	Have not adopted quantitative gw quality standards so use Federal dw standards. Delaware Comprehensive Groundwater Management Profile: Title 16, Section 122 (3) (c) Delaware Code Subsection 22.601.
Illinois None- see web site in reference	10 mg/L	Title 35 of IL Administrative Code, Subtitle F, Chapter 1, Part 260; www.ipcb.state.il.us/title35/download/F620.pdf.
Indiana Rob Ducan, (317) 308-3322	10 mg/L	Statute IC 13-18-17-5 and IC 13-18-4.
Kentucky Larry Taylor, (502) 564-6120	10 mg/L 16 mg/L	Personal communication with Larry Taylor. Use Federal MCL of 10 mg/L for cleanup purposes. Also have a Risk-Based Screening Value of 16 mg/L based on human exposure.
Maryland Mike Sivak, (410) 631-3493	10 mg/L	No actual cleanup standards. If the gw is not a dw source, used a risk-based approach. Otherwise, we use the Federal dw MCL of 10 mg/L. DW MCLs: 26.04.01.06. GW Quality Standards & Aquifer Classifications: 26.08.02.08 & .09.

Survey of Nitrate Ground Water (GW) Standards by State

All concentrations are measured as Nitrate - Nitrogen unless otherwise stated

State and Name	Standard	References
Mississippi James Crawford, (601) 961-5354	10 mg/L	Same as Federal dw MCLs. Currently trying to update/change their gw standards, "Groundwater Quality Standards."
New Hampshire None- see web site in reference	10 mg/L	New Hampshire's ambient gw quality standards are equivalent to Federal MCLs. Title 50: Water management and Protection, Chapter 485C, Section 485-C:6. http://199.92.250.14/rsa/50/485-6-6.htm .
New Jersey None- see web site in reference	10 mg/L	"Groundwater Quality Standards" (NJ A.C. 7:9-6). http://www.state.nj.us/dep/dwq/pdf/njac79-6.pdf .
New Mexico Bart Faris, (505) 841-9466	10 mg/l	New Mexico Water Quality Act, NMSA Chapter 74 Article 6, Water Quality Control Commission Regulations, Standards for Ground Water
New York John Zambrano, (518) 457-6997	10 mg/L	"NY State Ambient Water Quality Standards & Guidance Values & Groundwater Effluent Limitations."
Ohio None- see web site in reference	10 mg/L	Rule 3745-300-08: "Generic Unrestricted Potable Use Standards" in accordance with Rule 3745-300-10 of the Administrative Code. http://www.epa.ohio.gov/derr/derrmain.html .
Oregon Kari Salis, (503) 731-4312	10 mg/L	Drinking water and gw standards are the same - 10mg/L

Survey of Nitrate Ground Water (GW) Standards by State

All concentrations are measured as Nitrate - Nitrogen unless otherwise stated

State and Name	Standard	References
Pennsylvania Stuart Reese, (717) 772-4018	10 mg/L	Land Recycling & Environmental Remediation Standards Act. Subchapter C, Section 250.30 (3) (4) - MSCs for groundwater. http://www.dep.state.pa.us/dep/deputate/airwaste/wm/landrecycling/MANUAL/Manual.htm .
Rhode Island Ernie Panciera, (401) 222-3961	10 mg/L 5 mg/L	For gw classified as dw (90% of the state), the MCL is 10 mg/L. There is also a preventive action limit of 5 mg/L. "Rules and Regulations for Groundwater Quality", Regulation 12-100-006.
South Carolina Tom Knight, (803) 898-4251	10 mg/L	GW and dw are the same. "State Primary Drinking Water Regulations"; R.61-58.
Tennessee Tom Moss, (615) 532-0170	10 mg/L	Same as Federal dw standards; no separate gw standards. "Maximum Contaminant Levels Under the Tennessee Safe Drinking Water Act" , Rule 1200-5-1 et al.
Vermont David Allerton, (802) 241-3408	10 mg/L	Gw and dw standards are the same, which is the same as the Federal MCL - 10 mg/L.
Virginia Allen Hammer, (804) 786-1766	Applicable by Physiographic Province: 0.5 or 5 mg/L	"Water Quality Standards" (9 VAC 25-260-5 et seq.).

APPENDIX C

Nitrogen Compound Contamination Examples

Nitrogen Compound Contamination Examples

State **Arizona**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Explosives		360		
	Ground Water	Electronics		680		
	Surface Water	Explosives	Stream, Lake, Pond	1100		
	Waste	Explosives	Waste	3470		

State **California**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Unknown		1320		
	Ground Water	Fertilizer	Private Well	59		
	Ground Water	Military	Monitoring Well	140		
	Ground Water	Unknown	Monitoring Well	17		
	Ground Water	Military		14		
	Soil	Military		731		

State **Colorado**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Chemical Supplier	Monitoring Well	16		
	Ground Water	Explosives	Private Well	1500		

State **Florida**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Waste	Landfill	Waste	90		

State **Illinois**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Landfill	Private Well	12		
	Surface Water	Nuclear	Stream, Lake, Pond	230		
	Surface Water	Nuclear	Stream, Lake, Pond	70		
	Waste	Nuclear	Other Liquids	1980		

State **Iowa**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Fertilizer	Public/Municipal Well	128		
	Ground Water	Unknown	Monitoring Well	353		
	Ground Water	Landfill	Monitoring Well	120		

State **Iowa** *(CONTINUED)*

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
Site 1	Ground Water	Fertilizer Sales	Monitoring Well			8200
Site 1	Soil	Fertilizer Sales	Soil Samples	570	850	1420
Site 2	Ground Water	Fertilizer Sales	Monitoring Well	460	1	461
Site 2	Soil	Fertilizer Sales	Soil Samples	1400	730	2130
Site 3	Ground Water	Fertilizer Sales	Monitoring Well	1100		
Site 3	Soil	Fertilizer Sales	Soil Samples	680	1	681
Site 4	Ground Water	Fertilizer Sales	Monitoring Well	510	1600	2110
Site 4	Soil	Fertilizer Sales	Soil Samples	110	850	1960
Site 5	Ground Water	Fertilizer Sales	Monitoring Well	1390	5260	6650

State **Kansas**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Unknown	Monitoring Well	344		
	Ground Water	Unknown	Private Well	40		

State **Louisiana**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Mining	Monitoring Well			
	Surface Water	Explosives	Stream, Lake, Pond			

State **Michigan**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Manufactur	Monitoring Well	1250		

State **Minnesota**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Education		18		

State **Montana**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Unknown	Private Well	31		

State **Nebraska**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Medical Supply		25		
Doniphan	Ground Water	Fertilizer Sales	Monitoring Well	1350	880	6950
Doniphan	Soil	Fertilizer Sales	Soil Samples	19300	20000	79800
Mitchell	Ground Water	Fertilizer Sales	Monitoring Well	3550	3950	7500
Mitchell	Soil	Fertilizer Sales	Soil Samples	6600	13000	19600

State **New Jersey**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Aerospace	Monitoring Well			
	Waste	Landfill	Leachate	404		

State **New Mexico**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Nuclear		219		
	Ground Water	Mining		33		
	Surface Water	Nuclear	Stream, Lake, Pond	35		
Albuquerque	Ground Water	Residential/ Dairy	Private Well	25		
Albuquerque	Ground Water	Fertilizer Application	Private Well	500		
Fort Gallup	Ground Water	Munitions	Monitoring Well	150		
Hobbs	Ground Water	Explosives	Monitoring Well	800		1100
Vado	Ground Water	Dairy	Private Well	250		252

State **New York**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Landfill		14		
	Ground Water	Landfill	Monitoring Well	16		
	Ground Water	Military	Private Well	17		

State **North Dakota**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
Bismarck	Ground Water	Agrichemical Supply	Monitoring Well	17400	17800	35200
Enderlin	Ground Water	Agrichemical Supply	Monitoring Well	691	510	
Lidgerwood	Ground Water	Agrichemical Supply	Monitoring Well	476	109	585
Lisbon	Ground Water	Agrichemical Supply	Monitoring Well	700		

State **North Dakota** (*CONTINUED*)

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
Oakes	Ground Water	Irrigation Impacts	Lysimeters	150		
Walhalla	Ground Water	Agrichemical Supply	Monitoring Well	1030	1380	2410

State **Ohio**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Unknown		135		

State **Pennsylvania**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Unknown	Monitoring Well	524		

State **South Carolina**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Manufacturing		40		
	Surface Water	Chemical Supplier	Stream, Lake, Pond	80		

State **South Dakota**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Transportation	Private Well	99		

State **Texas**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Explosives				

State **Utah**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Military		31		
	Ground Water	Smelter	Monitoring Well			
	Ground Water	Nuclear	Monitoring Well	198		
	Ground Water	Military		18		
	Surface Water	Smelter	Stream, Lake, Pond			

State **Washington**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Nuclear	Monitoring Well	559		
	Ground Water	Mining	Monitoring Well	121		

State **Wisconsin**

City	Contaminant	Source	Sample	NO3	NH3	Total N Conc (ppm)
	Ground Water	Landfill	Monitoring Well	1001		

APPENDIX D

ITRC Work Team Contacts, ITRC Fact Sheet, ITRC Product List, and Document Evaluation Survey

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